CRYSTALLIZATION MICRO-MECHANISM OF AMORPHOUS NI–P

by

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Submitted in partial fulfillment of the requirements

For the degree of Doctor of Philosophy

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CASE WESTERN RESERVE UNIVERSITY

May, 2017
Crystallization Micro-mechanism of Amorphous Ni–P

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Dedicated to My Husband Zhen Li
My Daughters Macie Li and Joanna Li
My Parents Zhinjun Zhan and Liping Gao
My Parents in Law Liming Li and Yingnan Fan
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Acknowledgements

0.1 Acknowledgements

Firstly, I would like to express my sincere gratitude to my advisor, Prof. Frank Ernst, for his continuous support during my PhD, for his immense knowledge, encouragement, enlightenment, passion, and patience. I could not have imagined a better advisor and mentor for my PhD.

Secondly, I would like to thank: Prof. Rohan Akolkar and Ms. Xinyu Liu, for their help with preparing samples and teaching me to operate electroless plating; Prof. Paul Voyles and Ms. Pei Zhang, for their kind help with FEM and insightful discussions; Prof. Matthew Willard and Dr. Maria Daniil, for their kind help with VSM and very helpful discussions; Prof. John Lewandowski for his insightful comments of my thesis, and Ms. Janet Gbur for her kind help with DSC.

My sincere thanks also goes to Dr. Zahra Vashaei and Prof. Ruigang Wang for the stimulating discussions and kind help; All of the SCSAM engineers for the help with operating the instruments in SCSAM; The colleagues in our group, for their insightful discussions, kind help, and all the fun we have in the last five years.

Special thanks to my husband Mr. Zhen Li for the sleepless nights we were working together to do electroless plating and for supporting me all the time; My parents, for their help with taking care of my two daughters Macie and Joanna, for supporting me spiritually throughout my life.

Last but not the least, I acknowledge Atotech Deuschland GmbH for financial support.
Abstract

Crystallization Micro-mechanism of Amorphous Ni–P

Abstract

by

XUN ZHAN

0.2 Abstract

The crystallization of near-eutectic amorphous Ni–P can be significantly retarded by alloying a small fraction of tungsten. Complimentary characterization techniques are applied to understand this phenomenon. DSC (differential scanning calorimetry) reveals the isochronal and isothermal crystallization kinetics. XPS (X-ray photoelectron spectroscopy) provides core-level electronic signatures of Ni, phosphorus and tungsten, which reflect SRO (short-range order) evolution during crystallization. FEM (fluctuation electron microscopy) provides the MRO (medium-range order) evolution during crystallization. TEM (transmission electron microscopy) provides high-spatial-resolution information on phase nucleation and spatial distribution of atom species. Physical theory has been developed by combining results of these techniques to explain the role of tungsten: Macroscopic aspect (energetics and kinetics), the presence of tungsten reduces the driving force and increases the activation energy.
for crystallization. Microscopic aspect (micro-mechanistics), the presence of tungsten probably reduces the free volume (hypothesis) due to large atomic radius ratios of $r_W/r_{Ni}$ and $r_W/r_{P}$; introduces tungsten atoms diffusion to segregate due to chemical potential difference of tungsten in different crystalline phases; involves the breaking of all of W–P bonds with high bond energy. Moreover, theoretical criteria of an effective metal X alloying to improve the thermal stability of M–ML (metal–metalloid) amorphous systems has been proposed. The criteria are: (1) Large negative heat of mixing among X, M and ML. (2) Minimum amorphous free volume by appropriate combination of $r_X$, $r_M$ and $r_{ML}$. (3) Large chemical potential difference of X in minor than in major crystalline phase. (4) Large X–ML and X–M bond energy. The criteria conclude on what other potential alloying elements will do, which has implications for fundamental science and technologies. In addition, magnetization curves of as-plated and tempered Ni$_{80}$P$_{20}$ and Ni$_{76}$W$_4$P$_{20}$ were measured by VSM (vibrating sample magnetometer). Alloying tungsten does not change the paramagnetism of amorphous Ni$_{80}$P$_{20}$, but decreases the saturation magnetization of Ni$_{80}$P$_{20}$ after crystallization.
1 Introduction

1.1 Motivation

Electroless plated near-eutectic amorphous Ni–P (P: 18 – 21 at.%) is widely used as buffer layer material for rigid-memory disc platters. It prevents the crystal structure and orientation of the substrate (Al alloy) from texturing subsequently deposited layers, especially the functional magnetic layer (Co alloy). It can also be polished to much better flatness than a polycrystalline material, because polycrystalline material would have anisotropy regarding etching/polishing attack. Whereas amorphous alloy is isotropic, and therefore will respond the same way everywhere to etching/polishing. Moreover, amorphous Ni–P is paramagnetic;\(^1\) it does not exhibit spontaneous magnetization and, therefore, does not interfere with the magnetization of the functional magnetic layer. However, amorphous Ni–P is unstable and – particularly at elevated temperatures during processing – tends to crystallize into a phase mixture with ferromagnetic properties that do interfere with those of the functional layer. Therefore, understanding the underlying physical principles and finding...
ways to improve thermal stability of amorphous Ni–P is of scientific as well as technological interest.

1.2 Approach

According to the empirical rules proposed by Inoue, the amorphous state is generally favored or stabilized by fulfilling the following criteria:

1. Multicomponent systems consisting of more than three elements.
2. Significant difference in atomic size ratios above about 12% among the three main constituent elements.
3. Large negative heats of mixing among the three main constituent elements.

Therefore, we aimed to improve thermal stability of amorphous Ni–P by alloying a third element. By following empirical rules and considering the likely impact of these elements on the ferromagnetic properties, compatibility with the conditions of electroless plating, we selected tungsten as alloying element.

To advance physical understanding of crystallization behavior and alloying effects, we fabricated layers of amorphous Ni–P and Ni–W–P alloys with the same phosphorous fraction by electroless plating as prototypical materials. The understanding of crystallization behavior has two aspects: kinetics and micro-mechanism. Crystallization kinetics not only reveals to what extent alloying tungsten improve thermal stability of amorphous
Ni–P, it also helps understanding the nucleation- and growth mechanism of crystallization. Crystallization kinetics of amorphous Ni–P and Ni–W–P were studied by DSC (differential scanning calorimetry). Micro-mechanism answers how atoms diffuse to crystallize and how tungsten atoms impact such process by analyzing and comparing crystallization products, atomistic structure and microstructure evolution during crystallization of Ni–P and Ni–W–P:

1. Crystallization products were studied by XRD (X-ray diffractometry) and TEM (transmission electron microscopy).
2. Amorphous atomistic structure includes two parts: SRO (short-range order) and MRO (medium-range order). SRO provides structural information of the nearest neighbor, while MRO provides structural information that extends to $\approx 2$ nm distance. SRO and MRO evolution were studied by XPS (X-ray photoelectron spectroscopy) and FEM (fluctuation electron microscopy), respectively.
3. Microstructure evolution were studied by TEM.

By a combined study of crystallization kinetics and micro-mechanism, we uncover the role of tungsten in retarding crystallization of amorphous Ni–P. The results provide general insights that are useful for identifying further alloying elements that are effective in retarding crystallization.

In addition, magnetization curves of as-plated as well as tempered Ni–P and Ni–W–P were measured by VSM (vibrating sample magnetometer) for technological interest.
Introduction

1.3 Literature Review

Ni–P alloys have been extensively studied since 1946. In general, Ni–P alloys are classified by the phosphorus concentration in three regimes: low phosphorus (2 – 7 at.%), medium phosphorus (8 – 17 at.%), and high phosphorus (> 18 at.%) alloys. It is accepted that low phosphorus alloys are Ni nanocrystallines with phosphorus segregating on the grain boundaries, while medium phosphorus alloys are mixture of Ni nanocrystallines and amorphous structure, and high phosphorus alloys exhibit fully amorphous structure. One explanation of such phenomena is phosphorus atoms disturbs the regular arrangement of Ni atoms.
To satisfy application requirements of amorphous and paramagnetic characteristics, the phosphorus concentration in Ni–P alloy should be higher than 18 at.%. Moreover, eutectic composition usually has the most stable supercooled liquid, and thus has the highest amorphous thermal stability in the whole composition range. In Ni-rich (P < 25 at.%) Ni–P system, the eutectic composition is 19.2 at.%, shown in Ni–P phase diagram in Fig 1.1. According to the literature, the phosphorus concentration of most stable amorphous Ni–P is in the range of 18—21 at.%, namely near the eutectic composition (denoted as Ni$_{80}$P$_{20}$ hereafter).

The thermal stability of Ni$_{80}$P$_{20}$ can be improved by co-plating a small fraction (< 5 at.%) of third element X, such as W, Mo, Re, Cu, Sn, Sb, etc. To eliminate the influence of different phosphorus concentration, we focused on Ni–X–P systems with phosphorus concentration near 20 at.%. Therefore, the following review of crystallization kinetics, micro-mechanism and magnetic properties is focused on Ni$_{80}$P$_{20}$ as well as ternary amorphous (Ni,X)$_{80}$P$_{20}$ systems.

### 1.3.1 Crystallization Kinetics

The thermal stability of amorphous alloys can be illustrated by a TTT (time temperature trasformation) diagram, shown in Fig 1.2. Higher thermal stability means higher crystallization temperature $T_P$ at a specific heating rate during isochronal tempering, or longer incubation time $t_S$ at a specific temperature during isothermal tempering. The crystallization
Figure 1.2. Schematic TTT diagram of amorphous alloys.\textsuperscript{13}

Figure 1.3. (a) Isothermal DSC curves of Ni\textsubscript{80}P\textsubscript{20} at different temperatures $T$.\textsuperscript{16} (b) JMAK plot of Ni\textsubscript{80}P\textsubscript{20} tempered at 579 K.\textsuperscript{16}

kinetics of Ni\textsubscript{80}P\textsubscript{20} were thoroughly studied by DSC for both tempering processes.\textsuperscript{7,8,12,14,15}

Figure 1.3a shows typical isothermal DSC curves of Ni\textsubscript{80}P\textsubscript{20},\textsuperscript{7,16} which exhibit single exothermic peaks/reactions after an incubation time $t_{S}$. 
With increasing temperature, $t_S$ decreases because of increased diffusivity. Assuming a heat flow proportional to the total mass of crystalline phases yields the volume fraction $\nu$ of the transformation as a function of time $t$. The crystallization kinetics can be described by the JMAK (Johnson-Mehl-Avrami-Kolgomorov) model for the fraction $\nu$ of transformed material,\textsuperscript{17} derived by assuming subsequent nucleation, growth, and impingement:

$$\nu[t] = 1 - \exp \left[ - \left( \frac{t}{t_R} \right)^n \right],$$

(1.1)

where $t_R$ is the time to $1 - 1/e$ completion and $n$ the Avrami index, which reflects the type (dimensionality) of the transformation.\textsuperscript{18} Usually, $n$ ranges between 1 and 4 and can be obtained by plotting $\ln[\ln(1 - \nu[t])^{-1}]$ versus $\ln[t/s]$, as seen in Fig 1.3b. Three distinct stages of crystallization are revealed. However, only the slope of the second stage can be safely used to analyze the crystallization mechanism – for the first and the last stage, the data suffer from too much uncertainty (peak broadening by temperature inhomogeneity). For Ni$_{80}$P$_{20}$, Avrami index $n$ ranges from 3.0 to 3.8.\textsuperscript{15,16} The Avrami index is very sensitive to amorphous structure. An amorphous Ni$_{80}$P$_{20}$ with pre-existing crystalline nuclei, introduced by different synthesis conditions, shows smaller $n$ than that without pre-existing crystalline nuclei.\textsuperscript{19} It should be mentioned that Avrami index can be influenced by data processing, such as the determination of baselines of DSC curves,\textsuperscript{20} the incubation time,\textsuperscript{21} etc.

Another important parameter describing isothermal crystallization kinetics is apparent activation energy $E_a$, which can be determined by
Arrhenius relation \[ t[\nu] = t_0 \exp \left( \frac{E_a}{RT} \right), \quad (1.2) \]

where \( t[\nu] \) is the time at volume fraction \( \nu \), \( t_0 \) is a constant, and \( R \) is the gas constant. \( E_a \) for isothermal crystallization of Ni\(_{80}\)P\(_{20}\) is \( \approx 240 \) kJ/mol.\(^{16}\)

Isothermal crystallization \( E_a \) is also very sensitive to amorphous structure.

The thermal stability of amorphous alloys can also be studied by isochronal tempering. Fig 1.4a shows DSC curves of Ni\(_{80}\)P\(_{20}\) at different heating rates.\(^ {22}\) Single peaks representing exothermic reactions were observed. With increasing heating rate, the peak moves to higher temperature because of hysteresis atom diffusion. The characteristic temperatures \( T \), such as peak temperature \( T_p \) and start temperature \( T_s \), are related to the heating rate \( \beta \) by the Kissinger equation\(^ {23}\)

\[ \ln \left( \frac{\beta}{T^2} \right) = -\frac{E_a}{RT} + C, \quad (1.3) \]

where \( E_a \) is the apparent isochronal crystallization activation energy, \( R \) is the gas constant, and \( C \) is a constant. Fig 1.4b shows typical
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Kissinger plot of Ni$_{80}$P$_{20}$ with different characteristic temperatures. $E_\alpha$ for isochronal crystallization of Ni$_{80}$P$_{20}$ is $260-287$ kJ/mol$^{22,24}$ Kissinger analysis should only be applied to systems where $T_p$ is coincident with a constant value of fraction transformed,\textsuperscript{15} which may or may not be true for Ni$_{80}$P$_{20}$. Nevertheless, the measurements give reasonable values of $E_\alpha$ and have been widely used in crystallization kinetics study of isochronal tempering amorphous alloys.

Crystallization of Ni$_{80}$P$_{20}$ can be retarded by alloying a small fraction $f$ ($f < 5$ at.%) of third element that substitutes Ni, shown in Fig 1.5. Specifically, Krasteva,\textsuperscript{12} Antonelli,\textsuperscript{11} and we synthesized the amorphous alloys by electroless plating; Inoue,\textsuperscript{25} and Akatsuka,\textsuperscript{26} by melt spinning; Zhang,\textsuperscript{27} by rapid quench, respectively. The variation of different $T_p$ of
Ni$_{80}$P$_{20}$ at the same heating rate originates from different amorphous structure, which is essentially because of different synthesizing techniques and parameters. In general, ternary amorphous Ni–X–P all show relatively higher isochronal crystallization peak temperature $T_p$ than that of Ni$_{80}$P$_{20}$. However, the retarding crystallization effectiveness $e$ ($e = \frac{T_{\text{Ni-X-P}} - T_{\text{Ni-P}}}{f_x}$) of different alloying elements at the same heating rate are different. It can be seen that the rare earth elements show the highest $e$, while early transitional metals Hf, Zr, Ti, Nb, W show relatively lower $e$ than those of rare earth elements. Al shows similar $e$ as those of early transitional metals, and Cu, Sn, Sb show the lowest $e$. The different efficiency of retarding crystallization would be discussed latter in the thesis.

1.3.2 Crystallization Micro-mechanism

**Atomistic Structure.** To reveal the nature of crystallization behaviors of Ni–P and Ni–X–P, atomistic structure information is required. The atomistic structure of prototypical amorphous Ni$_{80}$P$_{20}$ has been extensively studied since the 1970s, including their SRO (short-range order) and MRO (medium-range order). Specifically, Cargill compared the measured PDF (pair distribution function) with the results of calculations based on Bernal’s DRPHS (dense random packing of hard spheres) model and obtained good agreement between experiment and simulation.$^{28,29}$ In the Bernal model, both Ni and phosphorous atoms are considered as hard
spheres of the same size, based on their similar Goldschmidt radii. However, this approach predicts a density that is smaller than that obtained by experimental measurement. Polk proposed that the Ni atoms follow a DRPHS configuration, while the phosphorous atoms reside in canonical holes. Unfortunately, this DRPHS model shows obvious inconsistencies of expected and experimentally observed intensity of PDF sub-peaks. The major problem of DRPHS models is that they ignore the relatively strong chemical order in amorphous Ni$_{80}$P$_{20}$, which has been confirmed by various kinds of experimental observations. Rather, those observations support the stereochemical model proposed by Gaskell. That model suggests that the SRO in amorphous alloys is well developed and almost identical to that in the corresponding crystals. The model implies that the main difference between amorphous and crystalline structure lies in the MRO, i.e., ordered versus random packing of stereochemical units. Gaskell proposed that the stereochemical unit for Ni–P is a TTP (tri-capped trigonal prism) with nine Ni atoms at the shell and one phosphorus atom in the center, as found in crystalline Ni$_3$P. Moreover, Gaskell suggested a chain-like connection of the TTP units by sharing edges.

Although the stereochemical model successfully reproduces the experimentally observed PDF, the unique stereochemical unit theory was overturned by later studies. Lamparter et al. simulated PPDFs (partial pair distribution functions) of Ni–P by a RMC (Reverse Monte Carlo) approach and found that distorted TTP can also fit the experimental PPDFs almost perfectly. Most recently, Sheng et al. proposed a model of efficient
packing of quasi-equivalent phosphorus-centered clusters by fitting experimental data of synchrotron XRD (X-ray diffractometry) and EXAFS (extended X-ray absorption fine structure) with the RMC and \textit{ab initio} MD (molecular dynamics) simulations\textsuperscript{34}, seen in Fig 1.6. That model confirms strong chemical order in amorphous Ni\textsubscript{80}P\textsubscript{20}: the SRO is dominated by Ni–P clusters, while P–P bonds are avoided. Moreover, the SRO is not necessarily the same as in crystalline Ni\textsubscript{80}P\textsubscript{20}, but determined by
the effective size ratio of Ni and phosphorus as well as the chemical composition. The SRO of amorphous Ni–P allows for intrinsic distortions and quasi-equivalent clusters. The MRO was proposed to correspond to dense random packing of these clusters, which usually have shapes approximating five-fold icosahedra and share outer Ni atoms.

The previously described experimental methods reveal mostly SRO information of amorphous alloys, but lack sensitivity for structural information at MRO length scales. Therefore, the simulations based on such experimental data as well as corresponding structure models mainly concern the SRO of amorphous Ni–P alloys. Recently, FEM (fluctuation electron microscopy), a TEM (transmission electron microscopy) technique to study MRO in amorphous materials,\textsuperscript{36,37} has been broadly applied to amorphous semiconductors,\textsuperscript{38} amorphous oxides,\textsuperscript{39} and metallic glasses.\textsuperscript{40–42} FEM can be performed by obtaining nanodiffraction patterns in STEM (scanning transmission electron microscopy) mode.\textsuperscript{43} With the electron beam rastering over the specimen, the local electron diffraction pattern intensity $I[k,r]$ is recorded as a function of diffraction (scattering) vector $k$ and location $r$. Adjustable parameters include the beam diameter, impacting the spatial resolution $R$ and the specimen thickness $h$, assumed to be constant over the field of view. The MRO and information on structure-heterogeneity can be obtained by calculating the normalized intensity variance

$$V[k,R] = \frac{\langle I[k,R,r]_r^2 \rangle_r}{\langle I[k,R,r]_r \rangle_r^2} - 1, \quad (1.4)$$
where $\langle \ldots \rangle_\mathbf{r}$ means the average over all sampling positions $\mathbf{r}$. Generally, if the sampling area is a single crystal, $V[\mathbf{k}, R] = 0 \forall \mathbf{k}$. If the specimen structure is perfectly ordered on a length scale of $R$, $V[\mathbf{k}, R]$ will show strong peaks at diffraction vectors $\mathbf{k}$ that fulfill Bragg conditions. On the other hand, $V[\mathbf{k}, R] = 0 \forall \mathbf{k}$ is also expected if the sampling area is ideally (completely random) amorphous.

Wen et al. simulated $V[\mathbf{k}]$ of Ni$_{80}$P$_{20}$ based on an MKA (modified Kob–Anderson) model and an ECP (efficient cluster packing) model. For both approaches, the simulated $V[\mathbf{k}]$ shows a well-developed peak at 4.8 nm$^{-1}$ and a weak peak at 8.3 nm$^{-1}$, seen in Fig 1.7. Both peaks are absent from the $V[\mathbf{k}]$ of liquid Ni$_{80}$P$_{20}$. However, corresponding experimental FEM data of amorphous Ni–P are not available for comparison.
Compared to amorphous Ni$_{80}$P$_{20}$, not much information is available on the atomistic structure of ternary amorphous Ni–X–P. One well-studied example is Pd$_x$Ni$_{(0.80-x)}$P$_{0.20}$, where $0.20 \leq x \leq 0.70$. Specifically, Alamgir et al. studied the effect of alloying on the chemical bonding and GFA (glass-forming ability) of Pd$_x$Ni$_{(0.80-x)}$P$_{0.20}$ by analyzing core-level binding energies of Pd, Ni, and phosphorus using XPS (X-ray photoelectron spectroscopy). They found that the atoms in the glassy and corresponding crystalline alloys generally have similar chemical environments, especially for the composition $x = 0.40$, which is known as the best glass former in the Pd–Ni–P system. Further, Alamgir et al. investigated the SRO around all three constituent atoms in amorphous Pd$_x$Ni$_{(0.80-x)}$P$_{0.20}$ by EXELFS (extended electron energy-loss fine structure) and EXAFS. They found that the environment of Pd in Pd-rich glass can be well described as that of Pd in crystalline Pd$_3$P. Similarly, the environment of Ni in amorphous Ni-rich Pd$_x$Ni$_{(0.80-x)}$P$_{0.20}$ is isostructural with that of Ni in crystalline Ni$_3$P. The crystal structures of Pd$_3$P and Ni$_3$P both have TTP structural units. For the best glass former, Pd$_{40}$Ni$_{40}$P$_{20}$, the environment of the metal atoms is a weighted average of the environments of Pd in Pd$_3$P and Ni in Ni$_3$P. The combination of the two SROs provides Pd$_{40}$Ni$_{40}$P$_{20}$ with good GFA.

Inoue and Hosokawa studied quaternary amorphous systems, particularly amorphous Pd–Ni–Cu–P. That system has even better GFA than Pd–Ni–P. To explain this, the authors suggested a MRO characterized by
coexistence of TTP and a structure unit corresponding to a tetragonal dodecahedron, introduced by alloying Cu.

**Crystallization Products.** Crystallization process of Ni$_{80}$P$_{20}$ has been extensively studied by many researchers. Some observed direct eutectic crystallization with stable products Ni (space group: Fm$ar{3}$m) and t-Ni$_3$P (space group: I$ar{4}$).$^{5,50–52}$ Others,$^{5,10,53–55}$ on the contrary, observed various sequences of crystallization, i.e., metastable phases form before/during the formation of stable Ni and t-Ni$_3$P. The reason of different reaction paths of Ni–P crystallization has not been addressed. Metastable phase(s) all show common X-ray diffraction peaks at 4.18 nm$^{-1}$, 5.20 nm$^{-1}$ and 5.29 nm$^{-1}$.$^{5,53,54,56}$ Controversy exists in identifying the metastable phases. Specifically, single phase Ni$_5$P$_2$,$^{5,54}$ Ni$_{12}$P$_5$,$^{53}$ as well as two phases Ni$_5$P$_2$ and NiP have been proposed as the metastable phase(s).$^{56}$

Fig 1.8a–e are simulated XRD patterns of t-Ni$_3$P,$^{52}$ RT-Ni$_5$P$_2$ (space group: P$ar{3}$c1) for low $T$ phase),$^{57}$ HT-Ni$_5$P$_2$ (space group: P6$_3$cm for high $T$ phase),$^{58}$ Ni$_{12}$P$_5$ (space group: I$4$/m),$^{59}$ and NiP (space group: Pbca),$^{60}$ respectively. These phases, however, are not the metastable phase formed during crystallization of Ni–P for three reasons: (1) The simulated XRD of the phases listed above do not match the three experimental peaks, although some researchers$^{5,54}$ suggest a solid solution of Ni in Ni$_5$P$_2$, forming Ni$_5$(P, Ni)$_2$, results in peaks shifts to match some of the three peaks. However, all the phases listed above are stoichiometric compounds with trace amount of Ni solubility based on Ni–P phase diagram in Fig 1.1. (2) The phases listed above are all phosphorus rich phases, while
Introduction

Figure 1.8. Simulated XRD patterns of, (a) t-Ni$_3$P, (b) RT-Ni$_5$P$_2$,\textsuperscript{57} (c) HT-Ni$_5$P$_2$,\textsuperscript{58} (d) Ni$_{12}$P$_5$,\textsuperscript{59} and (e) NiP\textsuperscript{60} in the range of 4.0—6.0 nm$^{-1}$.

...according to literature,\textsuperscript{5,50,51,53,54} they will finally decompose to stable Ni and Ni$_3$P phases, both of which are Ni rich phases. Such reaction is theoretically impossible to happen. (3) RT-Ni$_5$P$_2$ and Ni$_{12}$P$_5$ phases are equilibrium phases at room temperature shown in Ni–P phase diagram in Fig 1.1, and they will not decompose once they form. Therefore, the identity of the metastable phase(s) is still not clear. Since formation of metastable phase(s) influences crystallization kinetics of Ni$_{80}$P$_{20}$, we need to identify the phase and uncover its origin in this thesis.

Microstructure. Several TEM studies have been reported on the microstructure of Ni$_{80}$P$_{20}$ crystallization\textsuperscript{5,14,50,61,62}. For eutectic crystallization, formation of barrel-shaped spherulites (crystallites) of t-Ni$_3$P...
containing subgrains with a dispersion of Ni nanoparticles (Fig 1.9) was observed.\textsuperscript{5,50,63,64} Some authors have described the crystallization as classical nucleation and growth,\textsuperscript{5,14} however without detailed discussion of the atom transport required to generate the microstructure observed in crystallized Ni–P. Lu et al.\textsuperscript{61} in contrast, proposed (1) formation and growth of Ni\textsubscript{3}P precursor clusters and (2) crystal nucleation and growth by shearing and deposition of precursor clusters at the crystalline front. However, this model cannot explain specific features of the microstructure that have been observed in the crystallized phases.

Generally, a deeper understanding of the crystallization process can be obtained by analyzing ORs (orientation relationships) between the crystallizing phases. Earlier work by Watanabe et al. and Lu et al. reported preferred ORs (orientation relationships) in (Fe\textsubscript{40}Ni\textsubscript{40})(P\textsubscript{16}B\textsubscript{4}) and Ni\textsubscript{80}P\textsubscript{20}.\textsuperscript{50,61}
respectively. However, controversies exist regarding their exact nature, e.g. owing to overlapping spots in electron diffraction patterns. Watanabe et al. observed
\[ \text{OR-1:} \quad \langle 110 \rangle_{\text{BCT}} \parallel \langle 110 \rangle_{\text{FCC}} \]
\[ \wedge \quad \langle 001 \rangle_{\text{BCT}} \parallel \langle 112 \rangle_{\text{FCC}} \quad (1.5) \]
Lu et al. in contrast, found
\[ \langle 111 \rangle_{\text{BCT}} \parallel \langle 110 \rangle_{\text{FCC}}. \quad (1.6) \]
The parallelism (1.6), while not a complete OR, is incompatible with (1.5), as (1.5) implies a minimum angular deviation of \(19^\circ\) between any symmetry variants of \(\langle 111 \rangle_{\text{BCT}}\) and \(\langle 110 \rangle_{\text{FCC}}\).

Sui et al. observed the crystallization of amorphous \(\text{Ni}_{80}\text{P}_{20}\) produced by melt-spinning. For this Ni-rich near-eutectic alloy, they observed
\[ \text{OR-2:} \quad \langle 001 \rangle_{\text{BCT}} \parallel \langle 110 \rangle_{\text{FCC}} \]
\[ \wedge \quad \langle 110 \rangle_{\text{BCT}} \parallel \langle 111 \rangle_{\text{FCC}} \quad (1.7) \]
Similar to the crystallization process of \(\text{Ni}_{80}\text{P}_{20}\), both direct eutectic crystallization and various sequences of crystallization were also observed in crystallization of \(\text{Ni–X–P}\) (\(X: \text{Cu, W}\)). Eutectic crystallization of \(\text{Ni–Cu–P}\) and \(\text{Ni–W–P}\) form (\(\text{NiCu}\)) and t-\(\text{Ni}_3\text{P}\), (\(\text{NiW}\)) and t-\(\text{Ni}_3\text{P}\), respectively. On the contrary, various sequences of crystallization observes metastable phase(s) formation similar as the one(s) observed in \(\text{Ni}_{80}\text{P}_{20}\), namely common X-ray diffraction peaks at \(4.18\,\text{nm}^{-1}\), \(5.20\,\text{nm}^{-1}\) and \(5.29\,\text{nm}^{-1}\). The microstructures of crystallized \(\text{Ni–X–P}\) (\(X: \text{Cu, Mo, W}\)) were reported as formation of nano-crystallines.
1.3.3 Magnetic Properties

Magnetic properties of as-plated $\text{Ni}_{80}\text{P}_{20}$, and the change of magnetic properties of $\text{Ni}_{80}\text{P}_{20}$ during tempering is of vital importance to commercial application. As-plated $\text{Ni}_{80}\text{P}_{20}$ shows paramagnetic at room temperature.\(^9\) During isothermal or isochronal tempering, the precipitation of Ni (superparamagnetic or ferromagnetic, depending on the size of Ni precipitates\(^9\)) from paramagnetic matrix regardless of the accompanied Pauli paramagnetic $\text{t-Ni}_3\text{P}$ phase,\(^{69}\) leads to an increase of saturation magnetization. Fig 1.10 shows typical $M[T]$ of $\text{Ni}_{80}\text{P}_{20}$ at different heating rates.\(^{69}\) The change of magnetization is a result of two combined phenomena: (1) the precipitation of Ni during crystallization and (2) the change in Ni magnetization induced by increasing temperature.
The impact of small alloying additions of element X on the magnetic properties of Ni–P have been reported for X = Cu, Sn, Sb. Accordingly, all these ternary systems show paramagnetic in as-plated states. Ni–Cu–P and Ni–Sn–P exhibit lower saturation magnetization than Ni$_{80}$P$_{20}$, while Ni–Sb–P shows higher saturation magnetization than Ni$_{80}$P$_{20}$.
2 Experimental

2.1 Electroless Plating

Electroless plating is a process that involves reduction of complexed metal ions present in the electrolyte to form metallic deposits on the substrate of interest. This occurs in the absence of an externally applied voltage, and is mediated by a reducing agent also present in the electrolyte. Figure 2.1 shows the equipment for electroless plating. The potentiostat was connected to monitor the reactions in the solution by detecting the voltage between substrate and reference. Electrolytes were prepared

![Figure 2.1. Schematic of the setup for electroless plating.](image-url)
using analytic-grade reagents and deionized water. The volume of electrolytes for each bath is \( \approx 100 \) mL. The temperature of the electrolyte was kept constant at 368 K by circulating hot water through a heating jacket. Electroless plating was performed on a zincated-treated Al plate in the electroless solution. The immersion area of the zincated Al plate is \( \approx (1.5 \times 2) \) cm\(^2\). Before Ni–W–P plating, a 300 nm thick Ni–P layer was pre-plated onto the zincated Al plate to ensure a good adhesion between Al substrate and Ni–W–P layer.

### Table 2.1. Electroless Plating Parameters of Ni–P and Ni–W–P

<table>
<thead>
<tr>
<th>Sample</th>
<th>Chemical</th>
<th>Value / (mol m(^{-3}))</th>
<th>Operation Conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni–P</td>
<td>NiSO(_4)·7H(_2)O</td>
<td>100</td>
<td>pH=9, ( T=368 ) K</td>
</tr>
<tr>
<td></td>
<td>NaH(_2)PO(_4)·H(_2)O</td>
<td>200</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Na(_3)C(_6)H(_5)O(_7)·2H(_2)O</td>
<td>300</td>
<td></td>
</tr>
<tr>
<td>Ni–W–P</td>
<td>NiSO(_4)·7H(_2)O</td>
<td>37.5</td>
<td>pH=9, ( T=368 ) K</td>
</tr>
<tr>
<td></td>
<td>Na(_2)WO(_4)·2H(_2)O</td>
<td>75</td>
<td></td>
</tr>
<tr>
<td></td>
<td>NaH(_2)PO(_4)·H(_2)O</td>
<td>60</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Na(_3)C(_6)H(_5)O(_7)·2H(_2)O</td>
<td>300</td>
<td></td>
</tr>
</tbody>
</table>

Electroless plating parameters of Ni–P and Ni–W–P are summarized in Table 2.1. The Ni–P electroless solution consisted of nickel sulfate heptahydrate (NiSO\(_4\)·7H\(_2\)O), sodium hypophosphite monohydrate (NaH\(_2\)PO\(_2\)·H\(_2\)O) and sodium citrate dihydrate (Na\(_3\)C\(_6\)H\(_5\)O\(_7\)·2H\(_2\)O). NaOH and H\(_2\)SO\(_4\) were used to adjust solution initial pH. The partial reactions during Ni plating...
Experimental

\[ \text{Ni}^{2+} + 2e^- \rightarrow \text{Ni}, \quad (2.1) \]
\[ \text{H}_2\text{PO}_2^- + \text{H}_2\text{O} \rightarrow \text{H}_2\text{PO}_3^- + 2\text{H}^+ + 2e^- . \quad (2.2) \]

The Ni–W–P electroless solution consisted of sodium tungstate dihydrate (Na$_2$WO$_4$·2H$_2$O) in addition to those for Ni–P plating above. NaOH and H$_2$SO$_4$ were also used to adjust solution initial pH. The partial reactions during Ni and W plating are

\[ \text{Ni}^{2+} + 2\text{H}_2\text{PO}_2^- + 2\text{OH}^- \rightarrow \text{Ni} + 2\text{H}_2\text{PO}_3^- + \text{H}_2 , \quad (2.3) \]
\[ \text{WO}_4^{2-} + 6\text{H}_2\text{PO}_2^- + 4\text{H}_2\text{O} \rightarrow \text{W} + 6\text{H}_2\text{PO}_3^- + 3\text{H}_2 + 2\text{OH}^- , \quad (2.4) \]
\[ 2\text{H}_2\text{PO}_2^- \rightarrow \text{P} + \text{H}_2\text{PO}_3^- + 1/2\text{H}_2 + \text{OH}^- , \quad (2.5) \]
\[ \text{H}_2\text{PO}_2^- + \text{H}_2\text{O} \rightarrow \text{H}_2\text{PO}_3^- + \text{H}_2 . \quad (2.6) \]

The partial reaction during P plating for both Ni–P and Ni–W–P is unclear until now.

Due to bath instability during Ni–W–P plating, the bath pH was finely controlled by adding NaOH or H$_2$SO$_4$ solution manually every 5 min. In addition, the bath was changed every 4 h, since the growth rate of the Ni–W–P layer slowed down after long time plating with unknown reasons. The layer thickness after 4 h plating is $\approx 2\,\mu\text{m}$. Therefore, 5 baths and a total plating time 20 h were used to reach a 10 $\mu\text{m}$ Ni–W–P layer.
Table 2.2. XEDS Composition Quantification of as-plated Ni–P and Ni–W–P

<table>
<thead>
<tr>
<th>Sample</th>
<th>Ni / at.%</th>
<th>P / at.%</th>
<th>W / at.%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni–P</td>
<td>80.2 ± 0.1</td>
<td>19.8 ± 0.1</td>
<td>—</td>
</tr>
<tr>
<td>Ni–W–P</td>
<td>76.3 ± 0.5</td>
<td>19.9 ± 0.5</td>
<td>3.8 ± 0.1</td>
</tr>
</tbody>
</table>

2.2 Composition and Phase Identification

The as-plated materials were 10 µm thick layers, plated onto Al substrates. After dissolving the Al substrates in a 10% NaOH solution at 313 K, we punched out ϕ 3 mm discs for further study. The compositions were quantified by SEM (scanning electron microscopy)-based XEDS (X-ray energy-dispersive spectrometry). The measured compositions of the Ni–P and Ni–W–P layers are listed in Table 2.2. The phosphorus fractions of the Ni–P and Ni–W–P were (19.8 ± 0.1) at% and (19.9 ± 0.5) at%, i.e. practically identical. The Ni–W–P constitutes a solid solution in which tungsten atoms substitute for Ni atoms. On the length scale accessible to SEM-based XEDS (≈ 1 µm), the tungsten is uniformly distributed. Based on the compositions displayed in Table 2.2, we designate the composition of the Ni–P and the Ni–W–P as Ni$_{80}$P$_{20}$ and Ni$_{76}$W$_{4}$P$_{20}$, respectively.

XRD was performed on as-plated and tempered Ni$_{80}$P$_{20}$ and Ni$_{76}$W$_{4}$P$_{20}$ using a Bruker Discover D8 X-ray diffractometer, equipped with a Co-$K_{\alpha}$ monochromatic source ($\lambda = 0.17889$ nm). The peak positions were calibrated with the help of an Al$_2$O$_3$ reference sample.
2.3 Crystallization Kinetics

Isochronal and isothermal crystallization kinetics of Ni$_{80}$P$_{20}$ and Ni$_{76}$W$_{4}$P$_{20}$ were studied using a Netzsch Pegasus 404 F1 DSC system under pure Ar at a flow rate of 0.3 ml/s. Al pans with lids were used as sample holders. Temperature and enthalpy were calibrated by measuring the melting points and the heat of fusion of In-, Sn-, Bi-, and Zn standard specimens. Isochronal tempering were operated at four different heating rates: 0.08 K/s, 0.2 K/s, 0.3 K/s, 0.7 K/s. Isothermal tempering of Ni$_{80}$P$_{20}$ was operated at four different temperatures at a rate of 0.7 K/s: 583 K, 588 K, 593 K, and 598 K. Isothermal tempering of Ni$_{76}$W$_{4}$P$_{20}$ were also operated at four different temperatures at a rate of 0.7 K/s: 635 K, 640 K, 645 K, and 650 K. To study atomistic structure, microstructure and magnetization evolution, Ni$_{80}$P$_{20}$ and Ni$_{76}$W$_{4}$P$_{20}$ were held at 598 K and 650 K, respectively, for three different periods of time: 0.9 ks, 1.5 ks, and 2.4 ks. The corresponding stages are “incubation stage” (still completely amorphous), “partially crystalline” stage (amorphous and crystalline phases), and “completely crystalline” stage (only crystalline phases), respectively.

2.4 Atomistic Structure and Microstructure

XPS was performed on as-plated and tempered Ni$_{80}$P$_{20}$ and Ni$_{76}$W$_{4}$P$_{20}$ at room temperature using a VersaProbe (Physical Electronics, Inc., USA), equipped with an Al-K$_{\alpha}$ source (h$\nu$ = 1486.6 eV). To remove the oxide layer before spectrum acquisition, the samples were cleaned in situ by
Ar sputtering under conditions corresponding to high vacuum. The peak FWHM (full-width at half maximum) resolution was set to 0.7 eV, while the energy resolution for collecting the core-level photoelectrons was 0.2 eV. For energy calibration, we used the C-1s peak located at \((284.6 \pm 0.1)\) eV. The core-level binding energies of Ni-2p 3/2, P-2p 3/2, and W-4f 7/2 were determined by fitting the peaks using Multipak software.

TEM specimens were prepared from as-plated and tempered Ni\(_{80}\)P\(_{20}\) and Ni\(_{76}\)W\(_{4}\)P\(_{20}\). Final thinning to electron transparency was accomplished with a Tenupol 5 (Struers Inc.), using an electrolyte of 10 % HClO\(_4\) (perchloric acid) and 90 % CH\(_3\)-OH (methanol) at \(\approx 230\) K. Before FEM measurements, TEM specimens were plasma-cleaned with a 0.15 kPa Ar + O\(_2\) mixture for about 0.18 ks. In addition, completely crystallized Ni\(_{80}\)P\(_{20}\) and Ni\(_{76}\)W\(_{4}\)P\(_{20}\) TEM specimens were also prepared by Ar ion milling (Fischione 1010), using a voltage 4 kV, current 8 mA, and milling angle 12°. Final cleaning was carried out at a voltage of 0.2 kV, a current 8 mA, and a milling angle 9°.

FEM experiments were performed on a 200 kV Titan (FEI) (located at University of Wisconsin, Madison) equipped for STEM, including a spherical-aberration corrector for the probe-forming lens. The Schottky field-emission gun was operated at an extraction voltage of 4.5 kV. The instrument was operated in the “microprobe mode” with a probe diameter of 2 nm and a camera length of 512 mm in EFSTEM (energy-filtered STEM) mode with slit corresponding to energy window of 10 eV. A Gatan annular dark-field detector, mounted on the 2.5 mm GIF (Gatan Imaging
Filter) entrance aperture was used to collect STEM images simultaneously with the nanodiffraction patterns. The diffraction-lens current was adjusted using the FEI free-lens control interface to ensure good diffraction focus. 512 x 512-pixel² nanodiffraction patterns were acquired with a CCD (charge-coupled device) camera binning of 4 on a 10 x 10 grid of positions covering a 30 x 30 nm² area of the sample. Variance data from ten different areas of each sample were averaged together and are reported with one standard deviation of the mean error bars. The exposure time was set to 6 s in order to ensure a sufficiently high signal to noise ratio. The sample thickness was measured applying the log-ratio method to the elastic scattering transmittance. Since the tungsten fraction in the Ni₇₆W₄P₂₀ was only 4 at.%, we used the same elastic mean free path for Ni₈₀P₂₀ and Ni₇₆W₄P₂₀: 40 nm.⁴² The samples had an electron transmission rate of 50 to 60 %, thin enough for FEM study.⁷²

TEM studies of microstructures were conducted using a Tecnai F30 ST transmission electron microscope (300 kV, FEI) with a point resolution of 0.2 nm and an information resolution limit of 0.14 nm. The XEDS system of this instrument, combined with STEM nanoprobe capability providing a spatial resolution of about 2 nm, was used to study the elemental distribution in amorphous and crystalline phases.

2.5 Magnetic Properties

Magnetic properties of as-plated as well as tempered Ni₈₀P₂₀ and Ni₇₆W₄P₂₀ were studied using a LakeShore Model 7410 VSM system equipped with
oven. Magnetization curves ($M[H]$) of as-plated as well as tempered 
$\text{Ni}_{80}\text{P}_{20}$ and $\text{Ni}_{76}\text{W}_{4}\text{P}_{20}$ were measured at room temperature, with a 
magnetic field range $\pm 0.8 \text{ MA/m (}$±10 kOe$)$. 

To distinguish superparamagnetism from ferromagnetism, magneti-
ization curves of $\text{Ni}_{80}\text{P}_{20}$ and $\text{Ni}_{76}\text{W}_{4}\text{P}_{20}$ samples tempered at 598 K and 
650 K for 2.4 ks, respectively, were measured at three different temper-
atures, which are 300 K, 340 K, 380 K. The magnetic field range is also 
$\pm 0.8 \text{ MA/m (}$±10 kOe$)$. 


3 Results

3.1 Crystallization Kinetics

3.1.1 Isochronal Crystallization Kinetics

Figure 3.1 presents isochronal DSC curves of Ni$_{80}$P$_{20}$ and Ni$_{76}$W$_{4}$P$_{20}$ at different heating rates. Each curve exhibits one peak indicating an exothermal reaction – corresponding to the crystallization of amorphous
Ni$_{80}$P$_{20}$ and Ni$_{76}$W$_4$P$_{20}$. The integrated peak height reflects the total heat of the corresponding reaction – crystallization in this case. Comparing the integrals
\[ \int Q dt = \int \frac{\dot{Q}}{\beta} dT \] (3.1)
of the peaks at 0.3 K/s (20 K/min), where $\beta = \frac{dT}{dt}$, indicates that the heat of crystallization is $\approx 1.5$ times lower for Ni$_{76}$W$_4$P$_{20}$ than for Ni$_{80}$P$_{20}$. Similar phenomena are observed in other heating rates.

The peak in the curve from Ni$_{80}$P$_{20}$ corresponds to eutectic crystallization, forming Ni and t-Ni$_3$P. However, since a Ni–W–P ternary phase diagram is not available, the single exothermal peak in the curve from Ni$_{76}$W$_4$P$_{20}$ cannot simply be assigned to a corresponding eutectic reaction: In principle, it is possible that several reactions happen within the relevant temperature- and time intervals. According to XRD and TEM analyses in the following section, the peak in the curve from Ni$_{76}$W$_4$P$_{20}$ corresponds to formation of Ni, t-Ni$_3$P an h-Ni$_3$P. At the employed heating rates, Ni$_{76}$W$_4$P$_{20}$ shows higher crystallization temperature than that of Ni$_{80}$P$_{20}$. This is consistent with a previous study on Ni–W–P alloys with about 4 at.% W and 18 – 20 at.% P,\textsuperscript{11} although inconsistent with other studies in which several or one broad exothermal peak at lower temperatures were observed.\textsuperscript{10,56} Variations in peak position and shape originate from slight local variation of the chemical composition owing to limited control of plating conditions and corresponding slight local variation of the atomistic structure before crystallization.
Results

The apparent activation energies $E_a$ of isochronal crystallization of $\text{Ni}_{80}\text{P}_{20}$ and $\text{Ni}_{76}\text{W}_4\text{P}_{20}$ were obtained by Kissinger plots, shown in Fig 3.2. $\text{Ni}_{76}\text{W}_4\text{P}_{20}$ has a $E_a$ of $(465 \pm 40)$ kJ/mol, much higher than that of $\text{Ni}_{80}\text{P}_{20}$, $(290 \pm 9)$ kJ/mol. This suggests that alloying tungsten increases isochronal crystallization energy barrier of $\text{Ni}_{80}\text{P}_{20}$.

3.1.2 Isothermal Crystallization Kinetics

Figure 3.3 presents isothermal DSC curves of $\text{Ni}_{80}\text{P}_{20}$ and $\text{Ni}_{76}\text{W}_4\text{P}_{20}$ at different temperatures. The curves of both $\text{Ni}_{80}\text{P}_{20}$ and $\text{Ni}_{76}\text{W}_4\text{P}_{20}$ exhibit a single exothermic peak after an incubation time $t_5$. Each curve of $\text{Ni}_{80}\text{P}_{20}$ has good fitting with single Gauß function, corresponding to eutectic crystallization with formation of Ni and t-Ni$_3$P. Curve shapes of $\text{Ni}_{76}\text{W}_4\text{P}_{20}$ can not be simply represented by single Gauß function. Rather, it is a cumulative peak fitted by two Gauß functions, as seen in

![Figure 3.2. Kissinger plots of $\text{Ni}_{80}\text{P}_{20}$ and $\text{Ni}_{76}\text{W}_4\text{P}_{20}$.](image)

<table>
<thead>
<tr>
<th>Sample</th>
<th>Slope</th>
<th>$E_a$ (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Ni}_{76}\text{W}<em>4\text{P}</em>{20}$</td>
<td>$(56 \pm 5)$</td>
<td>$(465 \pm 40)$</td>
</tr>
<tr>
<td>$\text{Ni}<em>{80}\text{P}</em>{20}$</td>
<td>$(35 \pm 1)$</td>
<td>$(290 \pm 9)$</td>
</tr>
</tbody>
</table>
Figure 3.3. Isothermal DSC curves of, (a) Ni$_{80}$P$_{20}$ and (b) Ni$_{76}$W$_{4}$P$_{20}$ at different constant temperatures. Insets: fraction of crystallized volume as a function of time.

Figure 3.4. The single exothermal peak in the curve from Ni$_{76}$W$_{4}$P$_{20}$ cannot simply be assigned to a corresponding eutectic reaction: In principle, it is possible that several reactions happen within the relevant time intervals at a constant temperature. According to XRD and TEM analyses in the
Results

Figure 3.4. Isothermal DSC curves of Ni$_{76}$W$_4$P$_{20}$ fitted by two Gauß functions, named Peak 1 and 2, for each curve.

Figure 3.5. Ln[Ln[1 − ν[t]]$^{-1}$] plots of (a) Ni$_{80}$P$_{20}$ tempered at 598 K and (b) Ni$_{76}$W$_4$P$_{20}$ tempered at 650 K. Insets: Transformation volume fractions as a function of time.

Following section, Peak 1 corresponds to formation of Ni and metastable h-Ni$_3$P, while Peak 2 corresponds to formation of Ni and stable t-Ni$_3$P.

Ni$_{76}$W$_4$P$_{20}$ shows considerable $t_s$ at much higher annealing temperatures (650 K) than that of Ni$_{80}$P$_{20}$ (598 K). The volume fraction $\nu$ of
transformation as a function of time $t$ is shown in Fig 3.3 inset. Accordingly, $\ln[\ln(1 - v[t])^{-1}] - \ln[t]$ plots of $\text{Ni}_{80}\text{P}_{20}$ and $\text{Ni}_{76}\text{W}_{4}\text{P}_{20}$ tempered at $598 \text{ K}$ and $650 \text{ K}$, respectively, are shown in Fig 3.5. Three stages of crystallization are observed for $\text{Ni}_{80}\text{P}_{20}$, shown in Fig 3.5a. Stage 1 ends at about $1.4 \text{ ks}$, corresponding to a transformation volume fraction $0.4\%$. Stage 3 starts at about $2.5 \text{ ks}$, corresponding to a transformation volume fraction $97\%$. Therefore, the main stage is stage 2, covering the transformation volume fraction from $3\%$ to $97\%$. In stage 2, a linear fit gives the Avrami index $n = 3.7$, consistent with what is reported in the literature.\textsuperscript{15,16}

Three distinct stages of crystallization are also observed for $\text{Ni}_{76}\text{W}_{4}\text{P}_{20}$, shown in Fig 3.5b. Stage 1 ends at about $1.2 \text{ ks}$, corresponding to a transformation volume fraction $0.1\%$. Stage 2 ends at about $1.6 \text{ ks}$, corresponding to a transformation volume fraction $20\%$. Stage 3 starts at about $1.9 \text{ ks}$, corresponding to a transformation volume fraction $63\%$. Therefore, the main stages are stage 2 and 3. It is observed in the inset of Fig 3.5b that stage 2 corresponds to the major transformation of peak 1, namely formation of Ni and metastable h-Ni$_3$P, and that stage 3 corresponds to the major transformation of peak 2, namely formation of Ni and stable t-Ni$_3$P. Linear fits of stage 2 and 3 give the Avrami index $n = 3.4$ and $n = 3.1$, respectively.

The isothermal crystallization apparent activation energies $E_a$ of $\text{Ni}_{80}\text{P}_{20}$ and $\text{Ni}_{76}\text{W}_{4}\text{P}_{20}$ were obtained by Arrhenius plots, shown in Fig 3.6. $\text{Ni}_{76}\text{W}_{4}\text{P}_{20}$ has a $E_a$ of $(250 \pm 17) \text{ kJ/mol}$ at $50\%$ transformation volume
Fraction, higher than that of Ni$_{80}$P$_{20}$, (185 ± 3) kJ/mol. This suggests that alloying tungsten increases isothermal crystallization energy barrier of Ni$_{80}$P$_{20}$.

3.2 Crystallization Micro-mechanism

3.2.1 Short-to-Medium Range Order Evolution

XPS data of as-plated and tempered Ni$_{80}$P$_{20}$ and Ni$_{76}$W$_4$P$_{20}$, shown in Fig. 3.7, indicate the core-level electron binding energies of Ni-2p, P-2p, and W-4f. The binding energies of Ni-2p 3/2 in as-plated and tempered Ni$_{76}$W$_4$P$_{20}$ are all 852.9 eV, close to those of Ni$_{80}$P$_{20}$ (852.8 eV, 852.8 eV, and 852.7 eV, respectively). The corresponding P-2p 3/2 binding energies are all 129.6 eV, also similar to those of Ni$_{80}$P$_{20}$ (129.6 eV, 129.6 eV, and 129.4 eV, respectively). The binding energies of W-4f 7/2 are all 31.6 eV, consistent with those of metallic tungsten reported in literature.\(^73\)
Figure 3.7. XPS spectra of as-plated and tempered Ni$_{80}$P$_{20}$ and Ni$_{76}$W$_{4}$P$_{20}$ alloy. (a), (b), (c) P-2p, Ni-2p and W-4f core level of as-plated, tempered at 650 K 0.9 ks and 2.4 ks Ni$_{76}$W$_{4}$P$_{20}$, respectively. (d), (e) P-2p, Ni-2p core level of as-plated, tempered at 598 K 0.9 ks and 2.4 ks Ni$_{80}$P$_{20}$, respectively. (f) Table of peaks of P-2p 3/2, Ni-2p 3/2 and W-4f 7/2.

The spectra indicate that tungsten-alloying-induced energy shifts of core electron levels in Ni and phosphorus are no larger than the error limits of the measurements: $\approx 0.2$ eV. Moreover, crystallization does not induce core-level electron energy shifts of Ni, phosphorus, or tungsten. Since core-level binding energy shifts mainly originate from changes in next-neighbor interaction, altering core screening, the absence of (significant) peak shifts suggests that alloying 4 at% tungsten does not considerably change the statistical next-neighbor coordination of Ni- nor phosphorus atoms. Moreover, the crystallization process of both Ni$_{80}$P$_{20}$

<table>
<thead>
<tr>
<th>Sample</th>
<th>Ni-2p 3/2 (eV)</th>
<th>P-2p (eV)</th>
<th>W-4f 7/2 (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni-P as-plated</td>
<td>812.8</td>
<td>129.6</td>
<td>-</td>
</tr>
<tr>
<td>598 K 0.9 ks</td>
<td>812.8</td>
<td>129.6</td>
<td>-</td>
</tr>
<tr>
<td>598 K 2.4 ks</td>
<td>812.7</td>
<td>129.4</td>
<td>-</td>
</tr>
<tr>
<td>Ni-W-P as-plated</td>
<td>812.9</td>
<td>129.9</td>
<td>31.6</td>
</tr>
<tr>
<td>650 K 0.9 ks</td>
<td>812.9</td>
<td>129.9</td>
<td>31.4</td>
</tr>
<tr>
<td>650 K 2.4 ks</td>
<td>812.9</td>
<td>129.9</td>
<td>31.4</td>
</tr>
</tbody>
</table>
and Ni$_{76}$W$_4$P$_{20}$ does not significantly change the average atomistic environment of Ni, phosphorus, and tungsten.

Figure 3.8 shows $V[\mathbf{k}]$ for as-plated as well as for tempered Ni$_{80}$P$_{20}$ and Ni$_{76}$W$_4$P$_{20}$. These data were obtained with an electron microprobe diameter of 2 nm. The backgrounds of the curves were stripped by subtracting...
Figure 3.9. Diffraction patterns. (a) Typical nano-diffraction pattern shown 6-fold rotational symmetry in as received and tempered Ni$_{80}$P$_{20}$ and Ni$_{76}$W$_4$P$_{20}$ alloy. (b) Simulated diffraction pattern of NiO (111) zone axis.

fitted Lorentz function. The filled areas around the curves correspond to the standard deviations obtained by averaging over all sampling areas. Three peaks, located at 4.8 nm$^{-1}$, 6.7 nm$^{-1}$, and 8.3 nm$^{-1}$, are observed for all these alloys. The sharp peak at about 6.7 nm$^{-1}$, present in each curve, probably originates from electron diffraction at a nanocrystalline surface layer of NiO oxide (space group: Fm$\overline{3}$m). This is plausible for two reasons: (1) Deleting the nano-diffraction patterns containing spots with six-fold rotational symmetry (Fig. 3.9a) would result in a sharp drop of this peak height, while the other peaks are not influenced. (2) The spots with six-fold rotational symmetry show good match with the diffraction pattern expected from NiO for a (111) viewing direction, seen Fig. 3.9b. The hypothetical NiO layer was probably formed after final thinning of the TEM samples by electro-polishing. Deleting such patterns does not influence the variance values at other $k$. The hypothetical NiO layer has
an average thickness of only about 2 nm, determined by XPS using in situ Ar sputtering with a sputter rate of 1.6 nm/min. Therefore, the presence of the hypothetical NiO layer does not interfere with the analysis of MRO in Ni$_{80}$P$_{20}$ and Ni$_{76}$W$_{4}$P$_{20}$.

For amorphous Ni$_{80}$P$_{20}$ and Ni$_{76}$W$_{4}$P$_{20}$, the well-developed major peak at 4.8 nm$^{-1}$ as well as the weak peak at about 8.3 nm$^{-1}$ concur with a published calculation of $V[k]$ for Ni$_{80}$P$_{20}$ as metallic glass. In that work, the formation of these peaks was interpreted as the ordering of quasi-equivalent TTP Ni$_9$P clusters and the fluctuations accompanying such ordering. The position of the major peak is related to the nearest neighbor distance, and the nearly constant peak at 4.8 nm$^{-1}$ confirms that neither alloying 4 at% tungsten nor tempering significantly changes the average atomistic nearest-neighbor configuration.

The diffraction intensity variances of as-plated and those of tempered Ni$_{76}$W$_{4}$P$_{20}$ alloys are larger than those of corresponding Ni$_{80}$P$_{20}$ alloys. A higher variance indicates a larger structure fluctuation among regions within the typical sampling volume $\omega = r^2 \cdot t$ provided by the electron microprobe diameter of $2r \approx 2$ nm and the specimen thickness of $t \lesssim 30$ nm. The variation essentially reflects local variations of the excitation error, induced by deviation from perfectly ordered clusters. In other words, higher diffraction variance implies higher MRO.

During tempering, the maximum variance of amorphous Ni$_{80}$P$_{20}$ first decreases from $(4.6 \pm 0.5) \times 10^{-3}$ for as-plated Ni$_{80}$P$_{20}$ to $(2.4 \pm 0.3) \times$
Figure 3.10. FEM of Ni$_{80}$P$_{20}$ alloy in the $k$ range of 3.2 – 6.2 nm$^{-1}$. Gaussian functions were used to fit the $V[k]$ curve of Ni$_{80}$P$_{20}$ tempered at 598 K for 1.5 ks.

$10^{-3}$ for Ni$_{80}$P$_{20}$ tempered 0.9 ks at 598 K (remaining completely amorphous). The drop of variance indicates that brief tempering relaxes the initial amorphous structure of Ni$_{80}$P$_{20}$ into a less-ordered one. Extended tempering, 1.5 ks at 598 K, increases the variance to $(3.6 \pm 0.3) \times 10^{-3}$. At this stage, the Ni$_{80}$P$_{20}$ is partially crystalline. This variance increase indicates a corresponding increase of SRO, correlated with absorption of thermal energy. In addition to the major peak, Fig. 3.10 indicates two further peaks from the residual amorphous phase, which are located at $\approx 3.9$ nm$^{-1}$ and $\approx 5.7$ nm$^{-1}$ according to Gauß function fitting. The
corresponding regions are considered as nuclei of Ni$_3$P and Ni in the amorphous matrix, respectively, although calculations predict the peak corresponding to Ni$_3$P to occur at $\approx 3.3$ nm$^{-1}$. The difference between theoretical and experimental peak position probably arises from limitations of the underlying model of the calculations. The simultaneous nucleation of Ni$_3$P and Ni confirms that the crystallization of amorphous Ni$_{80}$P$_{20}$ occurs close to the eutectic composition.

In comparison, the maximum variance of as-plated amorphous Ni$_{76}$W$_4$P$_{20}$ slightly increases – from $(6.3 \pm 0.5) \times 10^{-3}$ for as-plated material to $(6.6 \pm 0.6) \times 10^{-3}$ and $(6.8 \pm 0.5) \times 10^{-3}$ for 650 K 0.9 ks and 1.5 ks tempered Ni$_{76}$W$_4$P$_{20}$ alloys, respectively. No structural relaxation is observed.

3.2.2 Crystallization Products

Figure 3.11a presents X-ray diffractograms of as-plated Ni$_{80}$P$_{20}$ and Ni$_{76}$W$_4$P$_{20}$ alloys. XRD captures the average SRO. Accordingly, both samples were amorphous. The positions and widths of the broad peaks characterizing XRD patterns are “finger prints” of the SRO. By isolating the total diffraction response from the instrumental background, one can obtain the PDF by Fourier transformation. Since the same experimental conditions were used to acquire XRD patterns of as-plated Ni$_{80}$P$_{20}$ and Ni$_{76}$W$_4$P$_{20}$, and the tungsten fraction of the Ni$_{76}$W$_4$P$_{20}$ was small, the instrumental background can be considered the same for both conditions. The similarity of diffractograms in the laboratory-source X-ray data, therefore, suggests nearly identical PDFs for both alloys, i.e. very similar
The XRD results are consistent with the XPS results. The crystallization products of Ni$_{80}$P$_{20}$ and Ni$_{76}$W$_4$P$_{20}$ tempered at 598 K and 650 K for 2.4 ks, respectively, were identified in Fig. 3.11b.
Accordingly, crystallization of Ni\textsubscript{80}P\textsubscript{20} forms stable Ni and t-Ni\textsubscript{3}P, with crystal structures shown in Fig 3.12. Crystallization of Ni\textsubscript{76}W\textsubscript{4}P\textsubscript{20} forms stable Ni, t-Ni\textsubscript{3}P, and unknown phase(s), which shows peaks at 4.18 nm\textsuperscript{-1}, 5.20 nm\textsuperscript{-1} and 5.29 nm\textsuperscript{-1} that cannot be attributed to these two phases. The origin of these peaks can be revealed by combining XRD with TEM-SAED (selected-area electron diffraction) (symmetry information) and STEM-XEDS (compositional information).

Figure 3.13 show TEM-SAED patterns of the unknown phase(s). Diffraction spots corresponding to 4.18 nm\textsuperscript{-1}, 5.20 nm\textsuperscript{-1} and 5.29 nm\textsuperscript{-1} in XRD pattern are observed. Specifically, diffraction spots of 5.20 nm\textsuperscript{-1} are observed in every pattern. Diffraction spots of 4.18 nm\textsuperscript{-1} and 5.20 nm\textsuperscript{-1} coexist in Fig 3.13d. Diffraction spots of 5.29 nm\textsuperscript{-1} and 5.20 nm\textsuperscript{-1} coexist
Results

Figure 3.13. TEM SAED patterns (black spots) and simulated electron diffraction patterns (blue circles) of h-Ni$_3$P.

in Fig 3.13e and g. The coexistence of these diffraction spots indicates that these peaks originate from a single phase.

The crystal system of the unknown phase can be obtained by analyzing the diffraction symmetry. SAED pattern in Fig 3.13a shows a three-fold or six-fold rotational symmetry, which is a typical symmetry feature of hexagonal, cubic, or trigonal crystal systems. Assuming the unknown crystal belongs to cubic system, the zone axis of Fig 3.13a is indexed as $\langle 111 \rangle$. The peak at 5.20 nm$^{-1}$ corresponds to $\{330\}$ planes, thus the lattice parameter of the cubic system is $a = 0.8159$ nm. On the other hand, according to Fig 3.13b, the smallest value of diffraction vector in this viewing direction is 1.45 nm$^{-1}$, smaller than that of $\{110\}$ planes (1.73 nm$^{-1}$). In cubic system, this diffraction vector corresponds to $\{100\}$
Results

planes. Therefore, the lattice parameter can also be calculated as $a = 0.6896\,\text{nm}$. The contradictory values of lattice parameter indicates that the crystal system of the unknown phase does not belong to the cubic system.

Based on Fig 3.13b, distinction of every other diffraction spot along vertical directions suggests the existence of $2_1$, $4_2$, or $6_3$ screw axis. Since the possible crystal system is hexagonal or trigonal crystal system, $2_1$ and $4_2$ screw axes can be ruled out. The existence of $6_3$ screw axis suggests a hexagonal crystal system. Due to strong dynamical diffraction effect of SAED, it is impossible to determine the space group of the unknown phase.

The compositional information of the unknown phase is shown in Fig 3.14. Fig 3.14a is TEM-BF (bright-field) image inside one grain of the unknown phase. The matrix is the unknown phase, with Ni nano-particles (micro-twinned) distributed inside the matrix. The dark region in Fig 3.14b, corresponding to the unknown matrix phase, has a composition close to $\text{Ni}_{75}\text{P}_{25}$ (Fig 3.14c). In addition, extra "Z contrast" besides the matrix and Ni nano-particles is also observed in Fig 3.14b, and its origin is discussed in the following section.

By combining symmetry and compositional information, we conclude that the extra peaks in XRD pattern originate from a single phase: $\text{Ni}_3\text{P}$ with a hexagonal structure, denoted as $h$-$\text{Ni}_3\text{P}$. The lattice parameters can then be calculated as $a = 0.666\,\text{nm}$ and $c = 1.375\,\text{nm}$. Hexagonal $\text{Ni}_3\text{P}$ has been proposed by Kuo and Ikari,\textsuperscript{74,75} and its lattice parameters
Figure 3.14. TEM BF image, corresponding STEM image and XEDS of one grain of unknown phase. (a) TEM-BF image showing diffraction contrast. (b) STEM image showing "Z contrast". (c) XEDS of region 1.

were calculated to be $\alpha = 0.672$ nm and $c = 1.428$ nm, or $\alpha = 0.656$ nm, $c = 1.392$ nm, respectively. Their results are similar to our calculation.

Moreover, we estimated a possible crystal structure of the hexagonal Ni$_3$P – a Fe$_3$N-type crystal structure with space group P6$_3$22. We applied the calculated lattice parameters, and substituted all the Fe, N atoms with Ni, P atoms, respectively, to construct a crystal structure of Ni$_3$P with P6$_3$22 space group. Based on this crystal structure, we simulated SAED, shown in Fig 3.13 (blue cirlces). The circles diameter
indicates the diffraction spot intensity. The larger the size, the higher the intensity. Perfect match of diffraction spot positions has been observed. However, because electron diffraction is strongly dynamical, diffraction spot intensities depend on the local specimen thickness and excitation conditions in a complicated way. Therefore, diffraction spot intensities do not directly reflect the corresponding structural factors, and SAED patterns are usually only evaluated with regard to spot positions, not spot intensities. In order to determine the space group, future work may employ CBED (convergent-beam electron diffraction) or micro-diffraction.

h-Ni$_3$P is not stable and will eventually transform to t-Ni$_3$P, which is stable. Based on the XRD pattern, we conclude that h- and t-Ni$_3$P form simultaneously. This means that stable t-Ni$_3$P can form directly from amorphous Ni$_{76}$W$_4$P$_{20}$. Metastable h-Ni$_3$P does not necessarily form during crystallization of Ni$_{80}$P$_{20}$ and Ni$_{76}$W$_4$P$_{20}$. Its appearance strongly depends on plating parameters, which influence details of the resulting atomistic structure.

By comparing the peaks of Ni and t-Ni$_3$P in XRD patterns of Ni$_{80}$P$_{20}$ and Ni$_{76}$W$_4$P$_{20}$, no peak shift is observed within the detection limit. The absence of tungsten-related expansion of interatomic spacings suggests that neither the forming Ni nor the forming t-Ni$_3$P contain significant fractions of tungsten. This is inconsistent with other studies,$^{10,11}$ which concluded that tungsten dissolves into Ni. In terms of Fig 3.14c, h-Ni$_3$P also does not contain significant fractions of tungsten. The distribution
of tungsten in the crystallized phases is further analyzed in the following section, based on XEDS-STEM.

3.2.3 Microstructure Evolution

**Microstructure of Ni$_{80}$P$_{20}$.** TEM provides detailed information on microstructure evolution during crystallization. A typical feature of the microstructure transition of Ni$_{80}$P$_{20}$ during tempering at 598 K is the formation of randomly orientated, micrometer-sized $\approx 5\,\mu m$ barrel-shaped $t$-Ni$_3$P grains with radially elongated subgrains, displayed in Fig 3.15. This feature is consistent with the results reported by other researchers.$^{50,62}$
Figure 3.16. TEM in ⟨001⟩ zone axis of t-Ni$_3$P. (a) TEM BF image. (b) SAED (lens-induced rotation versus image is not corrected for). Dashed lines indicate Ni reflections, circles indicate t-Ni$_3$P reflections. (c) HRTEM. (d) ESI phosphorus map.
Results

By viewing t-Ni₃P subgrains at high magnification, FCC (face-centered cubic) Ni nano-particles are identified by combining TEM-BF imaging, SAED, HRTEM (high-resolution TEM), and ESI (electron-spectroscopic imaging), as seen in Fig 3.16.

Figure 3.16a is a BF image of a few subgrains with \( \langle 001 \rangle_{Ni_3P} \parallel \langle 110 \rangle_{Ni} \) zone axis. In addition, the image reveals Ni nano-platelets with a typical length of 20 nm and a thickness of 5 nm. The split spots and “arcs” that appear in the diffraction pattern of Fig. 3.16b instead of sharp spots originate from a high density of structural defects – particularly small-angle grain boundaries and corresponding t-Ni₃P subgrain misorientations – within the selected area. (The rotation axes corresponding to these misorientations are not necessarily parallel to the viewing direction.)

Figure 3.16 reveals orientation variants of Ni nano-platelets that make 90° angles in the viewing direction. The HRTEM image in Fig 3.16c and the ESI elemental map of phosphorus (inset) confirm this. Similar observations were reported earlier.\(^{50,62}\) Figure 3.16b and c suggest that the BCT (body-centered tetragonal) and FCC lattices of Ni and t-Ni₃P in this region prefer the OR (1.7) described by Sui et al.:

\[
\text{OR-2: } \begin{align*}
\langle 001 \rangle_{BCT} & \parallel \langle 110 \rangle_{FCC} \\
\langle 110 \rangle_{BCT} & \parallel \{1\overline{1}1\}_{FCC}
\end{align*}
\] (3.2)
For t-Ni$_3$P subgrains larger than $\approx 0.1 \mu m$, HRTEM suggests the following preferred crystallographic IOs (interface orientations):

\[
\{110\}_{\text{BCT}} \parallel \{111\}_{\text{FCC}}, \quad (3.3)
\]

\[
\{110\}_{\text{BCT}} \parallel \{211\}_{\text{FCC}}. \quad (3.4)
\]

IO (3.3) corresponds to the extended (“long”) interface sections, while IO (3.4) is observed for the short sections. At both interfaces, the absolute value $|\delta|$ of the misfit

\[
\delta := 2 \frac{d_{\text{FCC}} - d_{\text{BCT}}}{d_{\text{FCC}} + d_{\text{BCT}}} \quad (3.5)
\]

between corresponding Ni- and t-Ni$_3$P lattice point spacings $d_{\text{FCC}}, d_{\text{BCT}}$ along the interface plane is small. The corresponding planes across the “short” interfaces (3.4) are $\{330\}_{\text{BCT}}$ and $\{111\}_{\text{FCC}}$, both normal to the interface plane. As quantitatively illustrated in Fig 3.18, this enables $\delta = -0.037$ (Ni spacings smaller). At the “long” interfaces (3.3), $\{330\}_{\text{BCT}}$ are matched by $\{111\}_{\text{FCC}}$ that are inclined against the interface plane by $70.5^\circ$. This enables an even smaller $\delta = +0.021$ (Ni spacings larger).

With this small misfit, the spacing of hypothetical $\mathbf{b} = \frac{1}{2}(110)_{\text{FCC}}$ misfit dislocations in Ni would be as large as $\approx 10 \text{ nm}$, about half of the typical length of the “long” interfaces observed in the HRTEM image and the phosphorus map of Fig 3.16c. This low density of misfit dislocations could significantly reduce the interface energy compared to competing ORs and IOs. In addition, the terminating layers of Ni$_3$P and Ni in the “long” interface sections correspond to low-indexed, densely-packed planes.
Results

\{110\}_{BCT} and \{111\}_{FCC}, respectively. Perpendicular to the viewing direction of Fig 3.16, however, OR-2, (3.2) implies \{004\}_{BCT} planes parallel to \{220\}_{FCC} planes. The misfit between the corresponding plane spacings is substantial: \(\delta = +0.126\).

The two orientation variants of Ni nano-platelets observed in Fig 3.16 originate from the different (incompatible) point symmetries of t-Ni\(_3\)P and Ni. The \{001\}_{BCT} viewing direction of Fig. 3.16 is parallel to two sets of equivalent \{110\}_{BCT} planes (dashed lines in Fig. 3.12b) making an angle of 90°, while the \{111\}_{FCC} planes of Ni that align themselves with the \{110\}_{BCT} planes according to (3.3) make an angle of only 70.5°. Therefore, if one set of \{111\}_{FCC} planes is parallel to either one set of \{110\}_{BCT}, there are two possible orientations for the second set of \{111\}_{FCC} planes in the \{110\}_{FCC} zone axis that is parallel to \{001\}_{BCT}.

Figure 3.12b shows that while the atomistic structure of t-Ni\(_3\)P has a lower symmetry than its BCT lattice, the atom configurations of the \{110\}_{BCT} and \{\overline{1}10\}_{BCT} planes are equivalent.

Figure 3.19 illustrates OR-2, (3.2) and compares it to OR-1, (1.5) by showing the relative orientation of the unit cells of Ni and t-Ni\(_3\)P drawn to scale. Actually, both ORs feature \{111\}_{FCC} parallel to \{110\}_{BCT}. The difference between OR-2, (3.2) and OR-1, (1.5) can be described as a 90° \{111\}_{FCC} rotation of the Ni lattice.

Figure 3.17 shows a set of TEM data equivalent to that in Fig 3.16, but from another region of the TEM specimen and in a different viewing direction: \{111\}_{BCT}, i.e. \{111\}_{Ni_3P} or \{\overline{1}11\}_{Ni_3P}. In this region, the HRTEM
Figure 3.17. TEM in (111) zone axis of t-Ni$_3$P. (a) TEM BF image. (b) SAED (lens-induced rotation versus image is not corrected for). Dashed lines indicate Ni reflections, circles indicate t-Ni$_3$P reflections. (c) HRTEM. (d) ESI phosphorus map.
Figure 3.18. Quantitative illustration of misfit at the Ni–t-Ni$_3$P interface. Top: OR-2, (3.2). Bottom: OR-3, (3.6).

Figure 3.19. Preferred ORs between the BCT unit cell of t-Ni$_3$P and the FCC unit cell of Ni.
image in Fig. 3.17c and the diffraction pattern in Fig. 3.17b indicate the
OR
\[
\text{OR-3: } \begin{align*}
\langle 111 \rangle_{\text{BCT}} & \parallel \langle 110 \rangle_{\text{FCC}} \\
\{1\bar{1}2\}_{\text{BCT}} & \parallel \{1\bar{1}1\}_{\text{FCC}}
\end{align*}
\] (3.6)
As seen in Fig 3.19, this result is incompatible with OR-1, (1.5) and OR-2, (3.2) (and all their symmetry-related variants). Instead, OR-3, (3.6) is compatible with the parallelism (1.6) observed by Lu et al.. Also, the corresponding orientations of the Ni lattices in OR-2, (3.2) and OR-3, (3.6) are not twin-related; this would require parallelism of \{111\}_{\text{FCC}} planes in Fig.3.19.

Further, Figure 3.17c reveals of preferred IOs that are different from (3.3,3.4):
\[
\begin{align*}
\langle 110 \rangle_{\text{BCT}} & \parallel \{211\}_{\text{FCC}} , \quad (3.7) \\
\langle 112 \rangle_{\text{BCT}} & \parallel \{111\}_{\text{FCC}} . \quad (3.8)
\end{align*}
\] The first one corresponds to “long” interfaces, the second one to “short” interfaces. At the “long” interface, the corresponding planes across the interface are \{111\}_{\text{FCC}} and \{112\}_{\text{BCT}}. As illustrated in Fig 3.18, their mismatch (3.5) is only $-0.019$. With this small $\delta$, similar to that implied by OR-2, (3.2) and (3.3), the spacing of hypothetical $b = \frac{1}{2}\langle 110 \rangle_{\text{FCC}}$ misfit dislocations in Ni would also be as large as $\approx 10$ nm, about half of the typical length of the “long” interfaces observed in the HRTEM image and the phosphorus map of Fig. 3.17c. At the “short” interface, corresponding planes are \{330\}_{\text{BCT}} and \{111\}_{\text{FCC}} inclined by $70.5^\circ$, as for OR-2, (3.2)
Figure 3.20. 3D configuration of Ni nano-particles in a t-Ni$_3$P grain.

with IO (3.3), enabling $\delta = +0.021$ (Fig. 3.18). Similarly low is the misfit between the corresponding $\{333\}_{BCT}$ and $\{220\}_{FCC}$ perpendicular to the viewing direction: $\delta = +0.035$. Since there is only one set of $\{11\overline{2}\}_{BCT}$ in the $\langle 111 \rangle_{BCT}$ viewing direction, all Ni nano-platelets are parallel in the BF and HRTEM image of Fig. 3.17.

In conclusion, Fig. 3.17 is not just a different view of the particles in the OR of Fig. 3.16, but evidence for the existence of at least two distinctly different preferred sets of ORs and IOs. Fig 3.20 illustrates several symmetry-related variants of Ni particles with these ORs and IOs. Both OR-2, (3.2) and OR-3, (3.6) were observed multiple times and with comparable frequency. Therefore, they appear to be preferred to similar extent. Adding further variety to the ORs between Ni and t-Ni$_3$P, the Ni nano-platelets can be internally twinned. Examples are seen in the HRTEM images of Fig. 3.21, which shows nano-platelets in a $\langle 110 \rangle_{FCC}$ viewing direction that corresponds to their long axis and in which the t-Ni$_3$P matrix does not produce lattice fringes with high contrast. The
Figure 3.21. HRTEM images of Ni nano-particles in t-Ni₃P. (a) Twinning in rod-like Ni particle. (The bright spots in the specimen hole at the bottom left are an artifact.) (b) Twinning in plate-like particle. Inset: ESI phosphorus map.
The cross-section of the particle in Fig. 3.21a more resembles that of a “rod.” The ESI phosphorus maps in Figs. 3.16 and 3.17, in which the Ni nano-particles appear as zero-intensity regions, also agree with a co-existence of rod-like- and platelet-like Ni nano-particles.

**Microstructure of Ni$_{76}$W$_4$P$_{20}$.** Figure 3.22 shows a TEM BF image revealing the typical microstructure transition of Ni$_{76}$W$_4$P$_{20}$ during tempering at 650 K. Grains with several $\mu$m diameter have formed from the amorphous matrix. Grains of similar size have also been observed in crystallizing Ni$_{80}$P$_{20}$ (Fig 3.15), however with significantly different typical...
Results

Figure 3.23. TEM BF image and HRTEM of Ni$_{76}$W$_4$P$_{20}$ alloy tempered at 650 K for 1.5 ks. (a) TEM BF image shows subgrains and nanoparticles in one grain. (b) HRTEM image of one nanoparticle in the grain.

shape: Those grains are always observed as spherulites, while in crystallized Ni$_{76}$W$_4$P$_{20}$, both spherulites and elongated grains are observed. The elongated grains are metastable h-Ni$_3$P, while spherulites can be either stable t- or metastable h-Ni$_3$P.

Similar details of the microstructure exist in both t- and h-Ni$_3$P grains. The typical microstructure in one grain is shown in Fig 3.23a, a conventional TEM BF image exhibiting diffraction contrast, i.e. regions with similar orientation show with similar image intensity. The different contrast at different regions suggests that subgrains exist in one grain. Within the grains, nanoparticles are observed. HRTEM identifies these as elemental Ni. Often, the Ni nanoparticles are internally twinned, as in the example shown in Fig 3.23b.
Figure 3.24. TEM BF image, SAED and HRTEM of t-Ni$_3$P grain with (001) zone axis in Ni$_{76}$W$_4$P$_{20}$ tempered at 650 K for 2.4 ks. (a) TEM BF image shows Ni nano-particles. (b) Corresponding SAED pattern. (c) HRTEM.
Figure 3.25. STEM image and XEDS in Ni$_{76}$W$_{4}$P$_{20}$ tempered at 650 K for 1.5 ks. (a) STEM image shows "Z-contrast". (b) XEDS of region 1 (dark contrast inside the grain), region 2 (bright contrast inside the grain) and region 3 (inside the amorphous matrix).

Figure 3.24a, b and c are TEM BF image, corresponding electron diffraction pattern and HRTEM of stable t-Ni$_3$P grain with ⟨001⟩$_{Ni_3P}||⟨110⟩_{Ni}$ zone axis, respectively. Fig 3.24a reveals orientation variants of Ni nano-platelets that make 90° angle in the viewing direction. This is similar to the microstructure of t-Ni$_3$P grain with ⟨001⟩$_{Ni_3P}||⟨110⟩_{Ni}$ zone axis in crystallized Ni$_{80}$P$_{20}$ alloy. Moreover, the electron diffraction pattern in Fig 3.24b exactly coincides with that of Ni$_{80}$P$_{20}$ alloy. Combining with HRTEM in Fig 3.24c suggests that the BCT and FCC lattices of Ni and t-Ni$_3$P in this region also prefer the OR-2, (3.2). In addition, the coincided electron diffraction pattern confirmed the XRD analysis that no significant Ni dissolves in Ni or t-Ni$_3$P.

**Where is tungsten?** This question can be answered by XEDS-STEM analysis. Fig 3.25a is the STEM image of Ni$_{76}$W$_{4}$P$_{20}$ tempered at 650 K for
1.5 ks. It reveals “Z-contrast” in the grain interior and in the amorphous matrix outside the grain. XEDS analysis (Fig 3.25b) showed that the dark region (region 1) inside the grain contains majorly Ni and phosphorus, with trace amount of tungsten. The composition is approximately Ni$_{75}$P$_{25}$, confirming the existence of Ni$_3$P with a tungsten fraction below 1 at%. The bright "jig-saw" region (region 2) inside the grain contains Ni, phosphorus, and tungsten. This region is rich in tungsten. The amorphous matrix region (region 3) contains Ni, phosphorus and tungsten, with composition similar as detected by SEM-XEDS. Combining these observations leads to the conclusion that tungsten segregates during crystallization, forming tungsten free Ni$_3$P region and W-rich region. Similar "Z-contrast" has also been observed in h-Ni$_3$P grains (Fig 3.14).

The W-rich region does not contribute significant diffraction intensity, and it is actually transitional or metastable state. Fig 3.26 reveals the microstructure of t-Ni$_3$P grain with $\langle 001\rangle_{\text{Ni}_3\text{P}} \parallel \langle 110\rangle_{\text{Ni}}$ zone axis in Ni$_{76}$W$_4$P$_{20}$ tempered at 650 K for 14.4 ks. After long time tempering, tungsten gradually dissolves into Ni, forming (NiW) solid solution, as seen in Fig 3.26d. In addition, W-rich regions have different Ni, tungsten and phosphorus concentrations, suggesting that these regions are not crystalline phases with certain crystal structure and stoichiometric composition, rather are transition zones from amorphous Ni-W-P to (NiW) solid solution and Ni$_3$P. Therefore, it can be predicted that after even longer time tempering, such W-rich transition zones would finally transform to equilibrium products (NiW) solid solution and t-Ni$_3$P.
Figure 3.26. TEM BF, STEM image and XEDS in one t-Ni$_3$P grain with (001) zone axis of Ni$_{76}$W$_4$P$_{20}$ tempered at 650 K for 14.4 ks. (a) TEM BF image shows diffraction contrast. (b) Corresponding STEM image shows "Z-contrast". (c) One specific region showing BF and corresponding STEM image. (d) XEDS of area 1,2, and 3.

The transformation can also be realized by heating to higher temperatures. Fig 3.27a-d present the crystallization phases of Ni$_{80}$P$_{20}$ and Ni$_{76}$W$_4$P$_{20}$ heated to 720 K, 690 K, 810 K, 910 K, respectively, at a heating rate of 0.167 K/s. Lorentz function was used to find the peak positions.
Figure 3.27. XRD patterns of Ni$_{80}$P$_{20}$ and Ni$_{76}$W$_{4}$P$_{20}$ heated to (a) 720 K, (b) 690 K, (c) 810 K, (d) 910 K, respectively, at a heating rate of 0.167 K/s. The XRD peaks were fitted by Lorentz functions.
of each phase. Fig 3.27a shows the formation of Ni and t-Ni$_3$P of Ni$_{80}$P$_{20}$ crystallization, with Ni {111} and {200} located at 52.03° and 60.72°, respectively. The calculated averaged lattice parameter of Ni according to Ni {111} and Ni 200 diffractions is $a = (0.3536 \pm 0.0003)$ nm. Fig 3.27b is the XRD pattern of Ni$_{76}$W$_4$P$_{20}$ heated to 690 K, higher than its $T_p$ at 0.167 K/s (Fig 3.1). It can be seen that metastable h-Ni$_3$P formed besides t-Ni$_3$P and Ni. In addition, the peak corresponding to Ni {111} is relatively broad, suggesting the formation of nano-sized Ni nano-particles. W-rich transition zones probably also contribute to the broadness of the peaks. Ni{111} peak locates at 51.88°, indicating a lattice parameter of $a = 0.3541$ nm. Fig 3.27c shows the XRD pattern of Ni$_{76}$W$_4$P$_{20}$ heated to 810 K. Metastable h-Ni$_3$P disappears, and Ni {111} peak becomes narrower, locating at 51.64°. The lattice parameter is then calculated as $a = 0.3557$ nm. Fig 3.27d shows the XRD pattern of Ni$_{76}$W$_4$P$_{20}$ heated to 910 K. Ni {111} peak becomes even narrower, locating at 51.21°. The averaged lattice parameter according to Ni {111} and {200} diffractions is $a = (0.3583 \pm 0.0002)$ nm. Therefore, the lattice parameter gradually increases from $a = (0.3536 \pm 0.0003)$ nm of Ni$_{80}$P$_{20}$ to $a = (0.3583 \pm 0.0002)$ nm of Ni$_{76}$W$_4$P$_{20}$. This means tungsten atoms gradually dissolves into Ni, forming (NiW) solid solution. Since tungsten has BCC (body-centered cubic) crystal structure, with lattice parameter $a = 0.3165$ nm, we can calculate the radius of tungsten atom as $r = 0.1370$ nm. Ni has FCC crystal structure, and its lattice parameter is $a = 0.3536$ nm based on our calculation, and thus the radius of Ni atom
Results

Figure 3.28. Magnetization curves of as-plated amorphous Ni$_{80}$P$_{20}$ and Ni$_{76}$W$_{4}$P$_{20}$ at room temperature. The signals from sample rod and Ag paste have been subtracted.

is $r = 0.1249$ nm. Applying Vegard’s law, the solid solution of tungsten into Ni for Ni$_{76}$W$_{4}$P$_{20}$ heated to 910 K can be estimated as 13.8 at.%. Considering the measurements error and the limitation of Vegard’s law, such value is close to the maximum solubility of tungsten in Ni at room temperature, i.e., $\approx 12$ at.%.  

3.3 Magnetic Properties

Figure 3.28 shows typical magnetization curves $M[H]$ of as-plated amorphous Ni$_{80}$P$_{20}$ and Ni$_{76}$W$_{4}$P$_{20}$ at room temperature. Linear $M[H]$ curves with positive susceptibility $\chi$ ($\chi \equiv M/H$) suggest para- or antiferromagnetic characteristics. According to literature, amorphous Ni$_{80}$P$_{20}$ is paramagnetic. Moreover, antiferromagnetic materials usually have a
Neel temperature $T_N$ far below room temperature, above which the substance is paramagnetic. Therefore, both Ni$_{80}$P$_{20}$ and Ni$_{76}$W$_4$P$_{20}$ are considered paramagnetic at room temperature. The room temperature mass susceptibility $\chi_{\rho}$ of Ni$_{80}$P$_{20}$ and Ni$_{76}$W$_4$P$_{20}$ are $1.6 \times 10^{-8}$ m$^3$/kg ($1.3 \times 10^{-6}$ emu/(g Oe)) and $1.2 \times 10^{-8}$ m$^3$/kg ($0.95 \times 10^{-6}$ emu/(g Oe)), respectively. Therefore, alloying 4 at.% tungsten does not fundamentally change magnetic behavior of amorphous Ni$_{80}$P$_{20}$.

Figure 3.29 are $M[H]$ curves of Ni$_{80}$P$_{20}$ and Ni$_{76}$W$_4$P$_{20}$ tempered at 598 K and 650 K for 0.9 ks, 1.5 ks, and 2.4 ks, respectively. Tempering for 0.9 ks, 1.5 ks, and 2.4 ks correspond to completely amorphous state, partially crystalline state, and completely crystalline state, respectively. The shape of a $M[H]$ curve is usually structure sensitive. Figure 3.29a and d show $M[H]$ curves of Ni$_{80}$P$_{20}$ and Ni$_{76}$W$_4$P$_{20}$ tempered for 0.9 ks, respectively. The typical hysteresis loops plus linear increases in $M[H]$ curves were observed. Although no Ni nano-particles were detected by XRD and TEM, the shape of the curves suggests that Ni-like clusters formed in the amorphous matrix. Similar features have also been observed in further tempered alloys, owing to the combined contribution to magnetization of Ni nano-particles and paramagnetic Ni$_3$P crystalline and/or paramagnetic amorphous matrix.

The mass magnetization at 0.8 MA/m (10 kOe) is close to the saturation magnetization, therefore, it can be considered as intrinsic parameter to compare. $M_\rho$ of 0.9 ks tempered Ni$_{80}$P$_{20}$ is 4 times larger than that of Ni$_{76}$W$_4$P$_{20}$, indicating more Ni-like clusters formation in Ni$_{80}$P$_{20}$ tempered.
Figure 3.29. $M[H]$ of Ni$_{80}$P$_{20}$ tempered at 598 K for (a) 0.9 ks, (b) 1.5 ks, (c) 2.4 ks and Ni$_{76}$W$_{4}$P$_{20}$ tempered at 650 K for (d) 0.9 ks, (e) 1.5 ks, (f) 2.4 ks. Insets: enlarged hysteresis loops at $H$ close to 0.

at 598 K for 0.9 ks than in Ni$_{76}$W$_{4}$P$_{20}$ tempered at 650 K for the same time period. On continued tempering, $M_\rho$ increases for both Ni$_{80}$P$_{20}$ and Ni$_{76}$W$_{4}$P$_{20}$, shown in Fig 3.30. Similarly, $M_\rho$ of Ni$_{80}$P$_{20}$ is 7 times larger than that of Ni$_{76}$W$_{4}$P$_{20}$. Two reasons contribute to the different $M_\rho$: (1) The volume fraction of Ni nano-particles in crystallized Ni$_{80}$P$_{20}$ is
Results

Figure 3.30. Mass magnetization of Ni$_{80}$P$_{20}$ and Ni$_{76}$W$_{4}$P$_{20}$ tempered at 598 K and 650 K for 2.4 ks, respectively, at magnetic field 0.8 MA/m (10 kOe).

Figure 3.31. $M[H]$ of, (a) Ni$_{80}$P$_{20}$ and (b) Ni$_{76}$W$_{4}$P$_{20}$ tempered at 598 K and 650 K for 2.4 ks, respectively, measured at different temperatures.

- Larger than that in crystallized Ni$_{76}$W$_{4}$P$_{20}$.
- Dissolving of tungsten into Ni nano-particles decreases the magnetization.

In addition, coercivity $H_C \approx 2$ Oe ($\approx 160$ A/m) and remanance magnetization $M_R \ 0.8 \% \ M_S$ were observed in each $M[H]$ curve. Such small $H_C$ and $M_R$ could be an artifact produced by measurement, i.e., it is possible that these curves show zero coercivity, which is a typical feature
of superparamagnetism. It has been well known that for superparamagnetism, magnetization curves measured at different temperatures (above blocking temperature $T_B$) superimpose when $M/M_S$ is plotted as a function of $H/T$. Moreover, such plot can be fitted by Brillouin function $B[J,x]$ according to Brillouin theory of paramagnetism,

$$B[J,x] = \frac{2J+1}{2J} \coth\left(\frac{2J+1}{2J}x\right) - \frac{1}{2J} \coth\left(\frac{x}{2J}\right),$$

(3.9)

where $B[J,x]$ is the normalized magnetization $M/M_S$. $J$ is the magnitude of vector addition of spin and orbital angular momentum, with the range of $J \in \left[\frac{1}{2}, \infty\right]$. When $J \to \infty$, Brillouin function reduces to classical Langevin function. $M_J$ is quantum numbers of $J$, with the range of $M_J \in [-J,J]$. During curve fitting, $M_J$ is usually set as $J$. $g$ is a dimensionless version of the gyromagnetic ratio. $\mu_0$ is permeability of free space. $\mu_B$ is Bohr magneton. $k_B$ is Boltzmann constant.
The $M[H]$ curves at three different measuring temperatures, 300 K, 340 K and 380 K of Ni$_{80}$P$_{20}$ and Ni$_{76}$W$_{4}$P$_{20}$ tempered at 598 K and 650 K for 2.4 ks, respectively, are plotted in Fig 3.31. The corresponding $M/M_S[H/T]$ plots are shown in Fig 3.32. The experimental data deviate from Brillouin function for both Ni$_{80}$P$_{20}$ and Ni$_{76}$W$_{4}$P$_{20}$, and the curves measured at three different temperatures do not overlap with each other. These suggest that it is not purely superparamagnetic responding. It is possible that this behavior reflects both superparamagnetism and ferromagnetism. Assume this is the case, therefore, part of the Ni nano-particles in Ni$_{80}$P$_{20}$ and Ni$_{76}$W$_{4}$P$_{20}$ have smaller volume that lead to the blocking temperature $T_B$ below room temperature, contributing to superparamagnetic behavior. While other Ni nano-particles have larger volume that result in $T_B$ higher than the measuring temperatures, contributing to ferromagnetic behavior.

To confirm this, we measured the Ni nano-particles particle-volume distribution by assuming particle shape as oblate ellipsoids ($a = b > c$) and assuming the measured particle length as 2$a$ of the oblate. The results are shown in Fig 3.33. The $T_B$ can be calculated by

$$
T_B = \frac{KV}{25k_B},
$$

where $V$ is particle volume, and $k_B$ is Boltzmann constant. $K$ is the total magnetic anisotropy energy density. Assuming that there are majorly magnetocrystalline anisotropy $K_C$ and shape anisotropy $K_S$, therefore, we can calculate the total magnetic energy density $E_{tot}$ by the sum of vectors
Figure 3.33. TEM BF images and particle-volume distribution of Ni nano-particles inside t-Ni$_3$P grain with (001) viewing direction. (a) and (c) Ni nano-particles, (b) and (d) volume distribution of Ni nano-particles in Ni$_{80}$P$_{20}$ and Ni$_{76}$W$_4$P$_{20}$ tempered at 598 K and 650 K for 2.4 ks, respectively.

$E_C$ (magnetocrystalline anisotropy energy density) and $E_S$ (magnetostatic energy density).$^{81}$ $K$ is then equal to the difference of maximum and minimum energy density $E_{\text{totmax}} - E_{\text{totmin}}$.

The magnetocrystalline anisotropy energy density $E_C$ for FCC Ni is$^{81}$

$$E_C = K_1 [(\alpha_1 \alpha_2)^2 + (\alpha_2 \alpha_3)^2 + (\alpha_3 \alpha_1)^2] + K_2 (\alpha_1 \alpha_2 \alpha_3)^2, \quad (3.12)$$
Figure 3.34. (a) Magnetocrystalline anisotropy energy surface $E_C$ of Ni. $x$, $y$, and $z$ are crystal axes (100), (010), and (001), respectively. (b) Magnetostatic energy surface $E_S$ of Ni. $a$, $b$, and $c$ are oblate axes.

where $K_1$ is $-4.5$ kJ/m$^3$, and $K_2$ is $2.3$ kJ/m$^3$, $\alpha_i$ are the direction cosines of the magnetization. The typical energy surface $E_C$ of Ni is shown in Fig 3.34a.

The magnetostatic energy density $E_S$ can be calculated\cite{81} by

$$E_S = \frac{1}{2} \mu_0 M_S \cdot N \cdot M_S,$$

where $N$ is the demagnetization tensor. For an oblate ellipsoid, $N = \begin{bmatrix} N_a & 0 & 0 \\ 0 & N_a & 0 \\ 0 & 0 & N_c \end{bmatrix}$, where $N_c$ is the demagnetizing factor for the hard direction (along $c$). $N_a$ is the demagnetizing factor for the easy direction (along $a$). $\mu_0$ is permeability of free space. $M_S$ is magnetization vector of FCC Ni,
Figure 3.35. (a) Ni total magnetic energy surface containing magnetocrystalline energy density $E_C$ and magnetostatic energy density $E_S$. (b) the total magnetic anisotropy constant $K = E_{\text{totmax}} - E_{\text{totmin}}$ at different $\gamma$. (c) Volumes of Ni oblates if $T_B = 300$ K at different $\gamma$.

1007 with $|M_S| = 484$ kA/m. The $N_c$ and $N_a$ of oblate ellipsoid are
1008
\begin{align}
N_c &= \frac{\gamma^2}{\gamma^2 - 1} \left( 1 - \frac{1}{(\gamma^2 - 1)^{1/2}} \times \arcsin \left( \frac{(\gamma^2 - 1)^{1/2}}{\gamma} \right) \right), \\
N_a &= \frac{1}{2(\gamma^2 - 1)} \left( \frac{\gamma^2}{(\gamma^2 - 1)^{1/2}} \times \arcsin \left( \frac{(\gamma^2 - 1)^{1/2}}{\gamma} \right) \right) - 1.
\end{align}

1009 where $\gamma = \frac{a}{c}$. A typical energy surface $E_S$ of an oblate is shown in Fig 3.34b, where $\gamma = 8.1$.

According to OR-2, (3.2), shown in Fig 3.18, the Ni oblate $c$ axis corresponds to Ni (111) crystal direction. Therefore, the total magnetic energy density can be calculated by aligning magnetostatic energy density accordingly in the crystal axes. A typical total energy density is shown in Fig 3.35a for $\gamma = 8.1$. The total magnetic anisotropy constant $K$, and the volume corresponding to a $T_B = 300$ K for different $\gamma$ is shown in Fig 3.35b and c.
According to Fig 3.33, the average $\gamma$ of Ni nano-particles in crystallized Ni$_{80}$P$_{20}$ and Ni$_{76}$W$_{4}$P$_{20}$ are 8.1 and 4.1, respectively. Therefore, in crystallized Ni$_{80}$P$_{20}$, $T_B = 300$ K requires the volume $V$ of the Ni nano-particle about 1000 nm$^3$. This means that Ni nano-particles with $V < 1000$ nm$^3$ can flip their magnetization direction several times as a result of thermal fluctuations during the room temperature measurement, i.e., superparamagnetic. Those with $V > 1000$ nm$^3$ have magnetization "blocked" at room temperature, i.e., ferromagnetic. The calculation proves the previous assumption of co-existence of both superparamagnetic and ferromagnetic Ni nano-particles in Ni$_{80}$P$_{20}$ tempered at 598 K for 2.4 ks.

In crystallized Ni$_{76}$W$_{4}$P$_{20}$, $T_B = 300$ K requires the volume $V$ of the Ni nano-particle about 1250 nm$^3$. Therefore, superparamagnetic and ferromagnetic Ni nano-particles also coexist in Ni$_{76}$W$_{4}$P$_{20}$ tempered at 650 K for 2.4 ks.

In summary, alloying tungsten does not change the paramagnetism of amorphous Ni$_{80}$P$_{20}$, but decreases the saturation magnetization of Ni$_{80}$P$_{20}$ after crystallization, probably owing to the formation of smaller volume fraction of superparamagnetic and ferromagnetic Ni nano-particles.
The crystallization of amorphous Ni$_{80}$P$_{20}$ and Ni$_{76}$W$_{4}$P$_{20}$ has two aspects: energetics and kinetics. The observed difference in the heat (3.1) of crystallization reveals that the presence of tungsten reduces the energetic advantage of the crystalline phases compared to the amorphous state, assuming that a small fraction of tungsten does not change the entropy significantly. In other words, the presence of tungsten reduces the driving force for crystallization. The impact of tungsten on crystallization kinetics can be understood by a careful analysis of the microscopic mechanism of crystallization, as discussed in the following section.

4.1 Crystallization Micro-mechanism

Crystallization involves the competition between amorphous phase and corresponding crystalline phase(s). Therefore, a comprehensive understanding of crystallization micro-mechanism requires the information of amorphous structure evolution and crystalline phase(s) formation during tempering.
4.1.1 Amorphous Structure Evolution

For the as-plated amorphous state, TEM and XEDS-STEM data presented earlier suggest that tungsten atoms are uniformly distributed down to nanometer length scale. Therefore, we hypothesize that tungsten is initially distributed in the most uniform way possible. In amorphous Ni$_{80}$P$_{20}$, according to previous study, the structure unit is quasi-equivalent Ni$_9$P TTPs similar to crystalline t-Ni$_3$P,\textsuperscript{33,34} as shown in Fig 4.1a. An important key to understand the observed effects of tungsten alloying, therefore, is how tungsten changes this structural unit in the as-plated amorphous structure. The XPS data indicate that – statistically – the atoms in amorphous Ni$_{80}$P$_{20}$ and Ni$_{76}$W$_4$P$_{20}$ have a similar environment of nearest neighbor atoms. Therefore, we hypothesize that tungsten is distributed by substituting for Ni in the Ni$_9$P TTPs. This hypothesis also makes physical sense considering the coordination of phosphorus.
In general, amorphous metal–metalloid alloys have strong SRO with atomistic structures similar to those of the corresponding crystalline phases. Applying this principle to a hypothetical amorphous $W_{0.80}P_{0.20}$, its structure unit would correspond to the tetragonal dodecahedron $W_8P$ shown in Fig 4.1b, which is the structure unit of crystalline $W_3P$ (space group: $I\bar{4}2m$). The atomistic environment of phosphorus in the Ni$_9P$ TTP and the $W_8P$ tetragonal dodecahedron are different. Therefore, if the structural unit of amorphous Ni$_{76}W_4P_{20}$ actually were the $W_8P$ tetragonal dodecahedron, one would expect a corresponding “chemical shift” of the phosphorus 2p binding energy in XPS spectra. However, we did not observe that. Since the tungsten fraction is only 4 at%, most structure units may contain no more than one tungsten atom, corresponding to a composition of Ni$_8WP$. Apparently, this level of Ni substitution by tungsten is not sufficiently high to favor the $W_8P$ tetragonal dodecahedron over a Ni$_8WP$ TTP as structure unit.

The ratio of Ni$_9P$ TTP to Ni$_8WP$ TTP in the amorphous Ni$_{76}W_4P_{20}$ can be estimated as follows: (1) The composition of Ni$_{80}P_{20}$ corresponds to a Ni:P ratio of 4:1. To realize this with Ni$_9P$ clusters, neighboring clusters have to share Ni atoms. If all of the Ni atoms were shared by 2, 3 or 4 P atoms, the composition would be Ni$_{4.5}P$, Ni$_3P$, or Ni$_{2.25}P$, respectively. Theoretically, Ni$_4P$ could combine all these conditions. Assume that out of all Ni atoms, $x_2$, $x_3$, and $x_4 = 9 - x_2 - x_3$ Ni atoms are shared by 2, 3, and 4 phosphorus atoms, respectively, and that these items are denoted
as Ni2, Ni3, and Ni4. This leads to the following condition for \( x_2, x_3 \):

\[
\frac{1}{2} x_2 + \frac{1}{3} x_3 + \frac{1}{4} (9 - x_2 - x_3) = 4 \quad \wedge \quad x_2 + y_3 \leq 9
\]  

(4.1)

Solutions include \((x_2 = 6, x_3 = 3, 9 - x_2 - x_3 = 0)\) or \((x_2 = 7, x_3 = 0, 9 - x_2 - x_3 = 2)\). In other words, one Ni9P cluster may consist of 6 Ni2 and 3 Ni3 atoms, whereas another such cluster consists of 7 Ni2 and 2 Ni4 atoms. A large number of Ni9P clusters will probably contain a combination of these two variants. (2) The composition of Ni_{76}W_{4}P_{20} corresponds to a Ni:W:P ratio of 3.8:0.2:1. If all of the tungsten atoms substitute Ni2, Ni3 or Ni4, the tungsten fraction \( X_W \) should satisfy the relations

\[
\frac{\frac{1}{2} X_W}{\frac{1}{2} (6 - X_W) + \frac{1}{3} \cdot 3} = q, \quad (4.2)
\]

\[
\frac{\frac{1}{3} X_W}{\frac{1}{3} (3 - X_W) + \frac{1}{2} \cdot 6} = q, \quad (4.3)
\]

\[
\frac{\frac{1}{4} X_W}{\frac{1}{4} (2 - X_W) + \frac{1}{2} \cdot 7} = q, \quad (4.4)
\]

respectively. \( q \) is W:Ni ratio, which is equal to \( \frac{0.2}{3.8} \). The solutions are\( X_W = 0.4, X_W = 0.6, \) and \( X_W = 0.8, \) respectively. In other words, if all tungsten atoms substituted for Ni2, Ni3, or Ni4, there would be 40\%, 60\%, or 80\% Ni_{8}WP clusters in amorphous Ni_{76}W_{4}P_{20}, respectively. As all these substitutions are possible, the fraction of Ni_{8}WP clusters will range between 40\% and 80\%. 

Discussion
Now consider the spatial arrangement of Ni$_8$WP and Ni$_9$P TTP clusters. Based on our FEM study, amorphous Ni$_{76}$W$_4$P$_{20}$ has a similar $V[\mathbf{k}, R]$ as amorphous Ni$_{80}$P$_{20}$. The peak at $\approx 4.8 \text{ nm}^{-1}$ in $V[\mathbf{k}, R]$ of Ni$_{80}$P$_{20}$ corresponds to the icosahedral arrangement of quasi-equivalent Ni$_9$P TTPs.$^{44}$ This suggests that the arrangement of Ni$_8$WP and Ni$_9$P TTPs also has icosahedral features. According to Miracle,$^{85}$ for a given coordination number, more efficient packing corresponds to smaller values of $R$ ($R$ is the radius of solute divided by radius of solvent atoms). Since the atomic radius of tungsten, 0.137 nm, is larger than that of Ni atom, 0.125 nm,$^{86}$ $R_W (r_p/r_W)$ is smaller than $R_{Ni} (r_p/r_{Ni})$. Therefore, Ni$_8$WP cluster probably has more efficient packing than Ni$_9$P cluster, and the icosahedral arrangement of Ni$_8$WP and Ni$_9$P clusters can possibly accomplish more complete space filling than the arrangement of just Ni$_9$P clusters. However, this conclusion is hypothetical, since we do not have direct experimental evidence for the space filling of Ni$_{80}$P$_{20}$ and Ni$_{76}$W$_4$P$_{20}$. This hypothesis implies less free volume available for diffusion and therefore more stable amorphous structure. This hypothesis also explains why structure relaxation was observed in as-plated amorphous Ni$_{80}$P$_{20}$, but not in as-plated amorphous Ni$_{76}$W$_4$P$_{20}$.

Another important aspect is the electron configuration of the alloying element, as it will impact the atomistic structure of P-centered clusters in amorphous Ni$_{80}$P$_{20}$ (or amorphous metal–metalloid alloys in general). For example, Ni and Pd belong to the same group of the periodic table and form similar P-centered clusters – Ni$_9$P and Pd$_9$P TTPs, respectively.
Tungsten and Mo are in the same group and have similar atomic radii as Pd. In crystalline $W_3P$ and $Mo_3P$, they form $W_8P$ and $Mo_8P$ tetragonal dodecahedra, respectively. Cu, which has a similar atomic radius as Ni, forms $Cu_8P$ tetragonal dodecahedra in crystalline $Cu_3P$. The fact that Pd–Ni–Cu–P has even better GFA than Pd–Ni–P has been interpreted as a result of co-existence between TTPs and tetragonal dodecahedron clusters instead of just TTPs in Pd–Ni–P.\(^2\) This theory suggests that a higher level of tungsten alloying, enabling the formation of $Ni_{8-x}W_xP$ tetragonal dodecahedra in addition to TTPs, would further stabilize the amorphous structure and retard the crystalline phase(s) formation to even higher temperatures. (However, the limit of this approach will be reached at alloying levels at which most structure units become tetragonal dodecahedra.) In a similar way, co-plating a fourth element that could form structure units other than TTPs could also have a strong effect on stabilizing the amorphous structure.

In summary, from amorphous structure point of view, alloying a small fraction of tungsten possibly results in denser icosahedral packing of quasi-equivalent TTPs clusters, hindering the rearrangement of clusters and the diffusion of atoms that are required for crystallization, and thus stabilizing amorphous state to higher temperature or longer time.

### 4.1.2 Crystalline Phases

The crystallization reaction of amorphous $Ni_{80}P_{20}$ is

$$Ni_{80}P_{20} \rightarrow t-Ni_3P + Ni,$$  \hspace{1cm} (4.5)
Discussion

namely eutectic crystallization forming t-Ni$_3$P grains and Ni nano-particles inside grains. The crystallization reactions of amorphous Ni$_{76}$W$_4$P$_{20}$ are

\[ \text{Ni}_{76}\text{W}_{4}\text{P}_{20} \rightarrow t\text{-Ni}_{3}\text{P} + \text{Ni} + \text{WZ}, \] (4.6)

\[ \rightarrow h\text{-Ni}_{3}\text{P} + \text{Ni} + \text{WZ}, \] (4.7)

\[ h\text{-Ni}_{3}\text{P} \rightarrow t\text{-Ni}_{3}\text{P}, \] (4.8)

\[ \text{WZ} + \text{Ni} \rightarrow t\text{-Ni}_{3}\text{P} + (\text{NiW}), \] (4.9)

where WZ means W-rich zones. The formation of metastable h-Ni$_3$P is not a necessary step; it can be suppressed by adjusting plating parameters. Moreover, metastable h-Ni$_3$P is a transition state during the transformation from amorphous state to equilibrium t-Ni$_3$P state. The existence of such transition state speeds up the crystallization kinetics, as seen in Fig 3.4, in which peak 1 (formation of h-Ni$_3$P) is ahead of peak 2 (formation of t-Ni$_3$P). Therefore, one option to increase the thermal stability of amorphous Ni$_{76}$W$_4$P$_{20}$ is to adjust plating parameters to obtain an amorphous structure that does not cause the formation of h-Ni$_3$P.

Table 4.1. Values of Nucleation Conditions $a$, Growth Conditions $b$, and Avrami Index $n^{87}$

<table>
<thead>
<tr>
<th>$a$</th>
<th>$b$</th>
<th>$n$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$a=0$, zero nucleation</td>
<td>$b=1$, 1D growth</td>
<td>$n=a+b$, linear growth</td>
</tr>
<tr>
<td>rate</td>
<td>$b=2$, 2D growth</td>
<td></td>
</tr>
<tr>
<td>$a=1$, constant nucleation rate</td>
<td>$b=3$, 3D growth</td>
<td>$n=a+0.5b$, parabolic growth</td>
</tr>
<tr>
<td>$a&gt;1$, increasing nucleation rate</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$0&lt;a&lt;1$, decreasing nucleation rate</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
To reveal the crystallization process in detail, we first discuss the Avrami index $n$. In general, Avrami index $n$ reflects isothermal crystallization type for metallic glass, and usually ranges from 1 to 4.\textsuperscript{18} $n$ has contributions from nucleation and growth conditions,\textsuperscript{87} denoted as $a$ and $b$, respectively. The values of $a$, $b$ and $n$ are summarized in Table 4.1. Avrami index $n = 3.7$ for Ni$_{80}$P$_{20}$ crystallization suggests most likely a homogeneous nucleation with decreased nucleation rate and 3D linear growth regime. Avrami index $n = 3.4$ and $n = 3.1$ for two stages crystallization of Ni$_{76}$W$_4$P$_{20}$ also suggest homogeneous nucleation with decreased nucleation rate and 3D linear growth regime for both stages. This indicates that nuclei do not pre-exist in as-plated amorphous Ni$_{80}$P$_{20}$ and Ni$_{76}$W$_4$P$_{20}$. Moreover, assuming that each stable nucleus eventually leads to the formation of t- and/or h-Ni$_3$P grain with subgrains and Ni nano-particles, the number density of nuclei is rather low (order of magnitude: $10^{16}$ m$^{-3}$) for both Ni$_{80}$P$_{20}$ and Ni$_{76}$W$_4$P$_{20}$. On the other hand, the size of the grains indicates that the growth rate is relatively large. This means that at $T = 598$ K and 650 K for Ni$_{80}$P$_{20}$ and Ni$_{76}$W$_4$P$_{20}$, respectively, crystallization is controlled more by the energy barrier of nucleation than by atom mobility.

Now consider the nucleation of crystallites in Ni$_{80}$P$_{20}$. The microstructure shows two phases forming either as platelets or rods of the minor phase embedded in the parent phase during crystallization, which have also been observed in other eutectic ML–M amorphous systems after crystallization in the same range of homologous temperature (570 K to
720 K), such as Fe–B, (Fe Ni)–(B, P), etc.\textsuperscript{62,64,88} Moreover, this microstructure is also typical of binary eutectic crystalization from a melt, requiring cooperative nucleation and growth of two phases. Generally, a platelet-like shape can minimize the interface energy by maximizing the area of low-energy facets. A rod-like shape, on the other hand, can minimize transport distances and is likely to form under conditions of low mobility.

Assuming homogeneous nucleation of cubic particles with side length \(a\) and an internal structure of planar Ni–t-Ni\(_3\)P lamellae with period \(\lambda\), and ignoring the strain energy between the nucleus and amorphous matrix, the Gibbs energy (“free enthalpy”) of nucleation in the amorphous Ni–t-Ni\(_3\)P matrix is

\[
\Delta G = -a^3 \Delta g + 2a^2 \gamma \frac{a}{\lambda} + 6a^2 \sigma. \tag{4.10}
\]

\(\Delta g\) is the difference between the system’s volume-specific Gibbs energy in the amorphous state and the crystalline state. \(\gamma\) and \(\sigma\) represent the area-specific energy of the Ni–t-Ni\(_3\)P interface and effective area-specific energy of the interface the two phases make with the amorphous matrix (both assumed to be isotropic). The critical nucleus size, associated with maximum \(\Delta G\), i.e. \(\frac{d}{da}G = 0\), is

\[
\alpha^* = \frac{4\sigma}{\Delta g - \frac{2\gamma}{\lambda}}. \tag{4.11}
\]

This implies a nucleation energy barrier of

\[
\Delta G^* = \frac{32\sigma^3}{\left(\Delta g - \frac{2\gamma}{\lambda}\right)^2}. \tag{4.12}
\]
This shows quantitatively how the energy $\gamma$ and spacing $\lambda$ of Ni–t-Ni$_3$P interfaces reduce the crystallization driving force $\Delta g$ to an effective driving force $(\Delta g - 2\gamma/\lambda)$ and how this leads to a corresponding reduction of the nucleation barrier (linear in $\gamma$ and $1/\lambda$ for $\gamma/\lambda \ll \Delta g$).

For a rough estimate, assume $\lambda \approx 10$ nm and a typical value for the interface energy $\gamma \approx 0.5$ J/m$^2$, implying $2\gamma/\lambda \approx 1 \times 10^8$ J/m$^3$. A literature value for $\Delta g$ is $\approx 6.5$ kJ/mol, corresponding to $\approx 2.5 \times 10^8$ J/m$^3$. Accordingly, $2\gamma/\lambda$ is comparable to $\Delta g$, implying that the interface energy $\gamma$ has a strong impact on $\Delta G^*$. Correspondingly, the (classical) nucleation rate (number of nucleating particles per volume and time)$^{90}$

$$\dot{N} \propto \text{Exp} \left[ -\frac{\Delta G^*}{RT} \right], \quad (4.13)$$

decreases rapidly with increasing $\gamma$. ($R$ is the universal gas constant and $T$ the absolute temperature.)

While this model is not particularly realistic, it provides a basis for discussing the effect of crystallization temperature on Ni particle spacing $\lambda$ and Ni–t-Ni$_3$P ORs/IOs. On the one hand, $\lambda$ is energetically confined by $\Delta g$. Assuming that $\gamma$ does not depend on temperature, the minimum possible $\lambda$ is inversely proportional to $\Delta g$, which, in turn, is proportional to the undercooling $\Delta T = T_m - T$, where $T_m$ is the melting point. Both trends work to decrease the particle spacing with increasing $\Delta T$ (decreasing temperature). In the regime of small $\Delta T$, i.e. small $\Delta g$, the condition $2\gamma/\lambda \leq \Delta g$ requires large $\lambda$ and small $\gamma$, i.e. ORs that minimize the interface energy. In the regime of large undercooling, in contrast, the
constraint is more kinetic than energetic. In this case, $\lambda$ is more limited by atom mobility, while sufficient energy may be available for ORs/IOs that do not provide the absolute minimum of interface energy $\gamma$. The fact that we observe two different ORs/IOs, both generating interfaces with low but presumably different energies $\gamma$, indicates that the microstructure evolution we observe is controlled by energetic and kinetic constraints as well. The latter is consistent with the low crystallization temperature of 598 K, corresponding to only about one half of the absolute eutectic temperature.

Compared to what was reported in the literature, the growth rate in our study is high. The absence of significant Ni- and P-2p peak shift in the XPS spectra from amorphous regions in samples tempered at 598 K for different times suggests a correspondingly insignificant variation in the next-neighbor coordination within the error limits given by the sensitivity of our XPS data. This suggests that the quasi-equivalent Ni$_9$P TTPs as such do not change during tempering at $T = 598$ K. However, the arrangement of these “building blocks” could change easily by breaking Ni–Ni neighborhoods. This hypothesis is further supported by considering the details of the t-Ni$_3$P crystal structure, shown in Fig. 3.12. Each phosphorus atom is surrounded by nine Ni atoms. This is the same SRO as in the amorphous structure of eutectic Ni–P. However, different from the amorphous structure, each Ni atom is shared by three Ni$_9$P TTPs in t-Ni$_3$P, and the Ni$_9$P TTPs are organized in a BCT lattice (Fig. 3.12b), rather than in an icosahedral arrangement.
Considering all observations, we propose the following crystallization micro-mechanism of Ni$_{80}$P$_{20}$. Firstly, in near eutectic amorphous Ni$_{80}$P$_{20}$, Ni$_9$P TTPs exist with icosahedral arrangement. During tempering, the Ni$_9$P TTPs remain intact with slight adjust of Ni-P bond length and angle, but rearrange themselves in space to decrease the volume-specific Gibbs energy $g$. The preferred arrangement corresponds to a BCT lattice with each Ni atom shared by three Ni$_9$P TTPs. This will leave some of the Ni atoms outside the Ni$_9$P TTP with the minimum amount of Ni–P bond breakings. These extra Ni atoms constitute embryos of FCC Ni to be formed. As seen in Fig. 3.12b, the \{110\}_Ni$_3$P and \{110\}_Ni$_3$P, i.e. all \{110\}_BCT, contain only Ni atoms. This explains our observations (3.3) and (3.7) that in t-Ni$_3$P, \{110\}_BCT is a preferred IO for the “long” Ni–t-Ni$_3$P interface. The twins in the Ni nano-particles could be growth faults that form under the conditions of high driving force and limited mobility, or as shear faults to relax transformation stresses. The latter would explain why the HRTEM images of Figs. 3.16 and 3.17 do not show twinning in the viewing direction parallel to the highly coherent Ni–t-Ni$_3$P interfaces.

Figure 4.2 shows further details of the atomistic configuration of one t-Ni$_3$P \{110\} plane. The configuration of the Ni atoms corresponds to a stretched FCC \{111\}_Ni within average Ni–Ni distance of 0.265 nm – only slightly larger than Ni–Ni distance in FCC Ni, 0.249 nm. This explains (3.3), i.e. that on the Ni side of the long/preferred Ni–t-Ni$_3$P interface the favored interface plane is \{111\}_Ni. Moreover, the growth along the interface is readily accomplished by just moving Ni atoms over a short distance (a
Figure 4.2. Atomistic structure of $(\bar{1}10)_{\text{Ni}_3\text{P}}$. (a) $[110]_{\text{Ni}_3\text{P}}$ projection, revealing an atom configuration analogous to $\{111\}_{\text{Ni}}$. (b) $[001]_{\text{Ni}_3\text{P}}$ projection. Enlarged are two regions of $(\bar{1}10)_{\text{Ni}_3\text{P}}$ with atom configurations corresponding to distorted hexagons.

small fraction of the lattice parameter) parallel to the interface. Growth of Ni normal to the interface, in contrast, is difficult: It requires cooperative movement of Ni$_9$P TTPs polyhedra. This provides another reason why the observed Ni precipitates have a large aspect ratio: in addition to the energetic advantage provided by low-energy Ni–t-Ni$_3$P interfaces, the extended shape provides a kinetic advantage.

This model can also explain the subgrains observed in the t-Ni$_3$P grains. Owing to the lack in directionality of the interaction between
neighboring Ni atoms, adjacent t-Ni$_3$P crystals sharing Ni atoms can afford a small amount of rotation without breaking Ni–P bonds. Similar observations were reported for the crystallization of amorphous Fe$_{80}$B$_{20}$ and Fe$_{40}$Ni$_{40}$P$_{14}$B$_6$, which means that the model proposed here can also explain the crystallization process in that system – and possibly others.

The crystallization of Ni$_{76}$W$_4$P$_{20}$ shares many similarities with that of Ni$_{80}$P$_{20}$. The analyses of nucleation and growth process of Ni$_{80}$P$_{20}$ can be applied to that of Ni$_{76}$W$_4$P$_{20}$ to some extent. Specifically, the microstructure typical of eutectic crystallization is observed, with two phases forming either as platelets or rods embedded in the parent phase during crystallization. The FCC Ni nano-particles show similar ORs with t-Ni$_3$P as those in crystallized Ni$_{80}$P$_{20}$, suggesting both energetic and kinetic constraints of crystallization. In addition, the growth rate of t-Ni$_3$P grains is also high. The absence of significant Ni- and P-2p peak shift in the XPS spectra in samples tempered at 650 K for different times also suggests a correspondingly insignificant variation in the next-neighbor coordination within the error limits of XPS measurement. This suggests that the quasi-equivalent Ni$_9$P and Ni$_8$WP TTPs do not change significantly during tempering at $T = 650$ K. Therefore, similar as in Ni$_{80}$P$_{20}$, Ni$_9$P TTPs rearrange in a BCT lattice with minimum breaking of Ni–P bonds.

However, there is one obvious difference: the redistribution of tungsten. According to our previous observations, tungsten distributes uniformly in amorphous matrix, while tungsten segregates in crystalline phases: tungsten diffuses out of t-Ni$_3$P lattice, forming W-rich transition
zones, and dissolves into Ni. This process is driven by chemical potential difference of tungsten in $t$-Ni$_3$P and in FCC Ni. The redistribution of tungsten suggests that all the W–P bonds need to be broken, and tungsten diffusion is required during crystallization, i.e., Ni$_8$WP TTPs, occupying 40—80% of total "building blocks", have to transform to Ni$_9$P TTPs. Therefore, comparing with crystallization of Ni$_{80}$P$_{20}$, that of Ni$_{76}$W$_4$P$_{20}$ contains not only the rearrangement of Ni$_9$P TTPs, but it also contains breaking of all W–P bonds and tungsten diffusion. The additional bond breakings and tungsten diffusion consume more thermal energy, leading to a higher thermal stability.

The chemical bonds between the involved atom species are an important aspect of retarding crystallization. It is known that amorphous Pd$_{40}$Ni$_{40}$P$_{20}$ is a good glass former, and its crystallization peak temperature $T_p$ is about 678 K at a heating rate of 0.33 K/s. However, compared to amorphous Ni$_{76}$W$_4$P$_{20}$, the retarding efficiency is not high. Already 4 at% tungsten retard the crystallization to about 687 K at the same heating rate. Pd and tungsten have nearly the same atom radius. Accordingly, different efficacies in retarding crystallization cannot be explained simply by steric aspects. The bond energy of solvent–solute also plays a role. The bond energy of M–P (metal–phosphorus) can be estimated by considering the mixing of binary M–P system

$$E_{MP} = \frac{\Delta H_{MP}}{P_{MP}} + \frac{1}{2} (E_{MM} + E_{PP}),$$

(4.14)
where $E_{MP}$ is the M–P bond energy. $\Delta H_{MP}$ is the heat of mixing between M and phosphorus. $E_{MM}$ and $E_{PP}$ are M–M and P–P bond energy, respectively. $P_{MP}$ is M–P bond fraction in the M–P system. Since tungsten and Pd have the same atom radius, the $P_{MP}$ can be considered the same. Calculations based on the Miedema model indicate that Pd has smaller heat of mixing with phosphorus, $-36.5 \text{ kJ/mol}$, than tungsten has with phosphorus, $-46.5 \text{ kJ/mol}$. Moreover, the metallic bond energy of tungsten $E_{WW}$ is $-859 \text{ kJ/mol}$, much higher than that of Pd, $-376 \text{ kJ/mol}$. Therefore, W–P bond energy is much larger than that of Pd–P, i.e. W–P bonds are stronger than Pd–P bonds. Since crystallization of Ni$_{76}$W$_4$P$_{20}$ requires breaking stronger W–P bonds than Pd–P bonds breaking during crystallization of Pd$_{40}$Ni$_{40}$P$_{20}$, tungsten atoms show higher retarding efficiency than Pd atoms.

In summary, from crystalline structure point of view, alloying a small fraction of tungsten involves breaking of strong W–P bonds as well as tungsten diffusion besides the rearrangement of quasi-equivalent Ni$_9$P TTPs, resulting in a higher required activation energy, thus retarding crystallization to higher temperature or longer time.

### 4.2 Role of Tungsten

Based on above discussion, we summarize the role of tungsten in retarding crystallization of Ni$_{80}$P$_{20}$ by introducing:

1. Denser atomic packing. Alloying tungsten introduces quasi-equivalent Ni$_8$WP TTP clusters in addition to quasi-equivalent
Ni$_9$P TTP clusters present in Ni$_{80}$P$_{20}$. These clusters arrange themselves in an icosahedral configuration similar to the arrangement of just Ni$_9$P TTP clusters. However, the substitution of Ni by tungsten with larger atomic radius provides a higher degree of space filling (hypothesis), thus reducing the free volume available for atoms diffusion, slowing nucleation and growth kinetics, stabilizing the amorphous state.

2. Tungsten transport. Tungsten has lower chemical potential in FCC Ni than in t-Ni$_3$P, leading to tungsten diffusion to segregate during crystallization. Tungsten diffusion needs more thermal energy than Ni diffusion because of the large radius of tungsten atoms. Therefore, the introducing of tungsten diffusion slows nucleation and growth kinetics, stabilizing the amorphous state.

3. Extra bond breaking. Alloying tungsten introduces W–P bonds in addition to the Ni–P bonds. The crystallization process involves all of W–P bonds breaking in addition to Ni$_9$P TTP clusters rearrangement and minimum Ni–P bonds breaking, which requires more activation energy for crystallization.

4.3 General Principles

We have already understood the role of tungsten in retarding crystallization of Ni$_{80}$P$_{20}$, now it is time to generalize the retarding effect. The corresponding discussion involves two aspects: (1) Theoretical criteria and (2) Technical aspects.
4.3.1 Theoretical Criteria

We propose the criteria of an effective metal X alloying to improve the thermal stability of M–ML (metal–metalloid) amorphous systems as

i. Large negative heat of mixing among X, M and ML.

ii. Minimum amorphous free volume by appropriate combination of \( r_X, r_M \) and \( r_{ML} \).

iii. Large chemical potential difference of X in different crystalline phases, implying the need for atom transport to reach thermodynamic equilibrium.

iv. Large X–ML and X–M bond energy.

For item 1, large negative heat of mixing among element X, M and ML ensures a uniform distribution of X in amorphous M-ML systems, which is a necessary condition to increase the thermal stability. For item 2, Minimum free volume restricts atoms diffusion. In the case of M–ML systems, which usually form ML centered clusters, minimum free volume usually requires the radius of X is larger than that of M atoms, i.e. a large atomic radius ratio \( r_X/r_{ML} \) or \( r_X/r_M \). For item 3, the chemical potential difference causes element X segregation, i.e. extra X atoms diffusion and X–ML bond breaking. The chemical potential difference can be estimated by looking at the solubility of element X in different crystalline phases. A higher solubility of X in one minor crystalline phase(s) than in major crystalline phase(s) can result in the segregation of X into the minor product, thus slow crystallization kinetics. For item 4, stronger bonding requires higher
thermal energy for bond breaking. The bond energy of X–ML and X–M can be estimated by 4.14. It should be emphasized that alloying element X here is focused on metal elements. For metalloid elements, the alloying would introduce alloyed-metalloid-centered clusters, and the crystallization micro-mechanism could be different.

Now we apply the criteria to find the most thermally stable Ni–X–P system (P: 18–21 at.%), where X is mainly transition- and semi-metals. Figure 4.3 summarizes the heats of mixing of X–P and X–P,\textsuperscript{86} the bond energies of X–X,\textsuperscript{93,94} and atomic radius ratio of $r_X/r_P$ and $r_X/r_{Ni}$.\textsuperscript{86} In general, most of the transition- and semi-metals can increase the thermal stability of Ni–P more or less. However, the effectiveness $e$ is quite different.

We first discuss element X1 (X1: Sc, Ti, V, Y, Zr, Nb, Hf, Ta). X1 have very large negative heats of mixing with phosphorus and Ni. In addition, the X1–X1 bond energies are relatively high, therefore, high X1–P bond energies can be estimated based on 4.14. X1 also have very large atomic radius, contributing to high atomic packing density. Moreover, the solubility of X1 in t-Ni$_3$P and Ni are negligible. This means that X1-rich phases should form during crystallization. Since only a small fraction of X1 are alloyed into Ni–P, the volume fraction of X1-rich phases would be low. Therefore, X1 satisfy all the requirements in the criteria, and should have high $e$.

Secondly, we discuss element X2 (X2: Mo, Tc, Ru, Rh, W, Re, Os, Ir, Pt). X2 have medium negative heats of mixing with phosphorus and
small negative/positive heats of mixing with Ni. In addition, the X2–X2 bond energies are extremely high, especially tungsten, which is the highest in the periodic table. Therefore, the bond energies X2–P are very
high, in spite of relatively lower heats of mixing compared with X1. X2 show relatively large atomic radius, thus relatively dense atomic packing. Moreover, the solubility of X2 in major phase Ni₃P are negligible. Ir and Ni are completely miscible. Rh, W, Re and Pt have solubilities in Ni larger than 10 at.%. Therefore, during crystallization, Ir, W, Re will gradually segregate into minor phase Ni. Mo, Tc, Ru, Os have negligible solubility in Ni, thus forming X2-rich minor phase. Therefore, high e are also expected for X2.

Thirdly, we discuss element X3 (X3: Fe, Co). X3 show medium negative heats of mixing with phosphorus and small negative heats of mixing with Ni, similar to X2. However, Fe, Co have almost the same atomic radius as that of Ni, which would not contribute to increasing packing density. In addition, X3 have similar or lower X3–X3 bond energies than that of Ni, which do not provide strong X3–P bonds. Moreover, Fe and Co can dissolve both in major phase Ni₃P and minor phase Ni, which do not involve alloying elements diffusion to segregate during crystallization. Therefore, X3 should have the lowest e.

Next, we discuss element X4 (X4: Al, Pd, Ag, In, Sn, Au, Tl, Pb, Bi). X4 show relatively small negative heats of mixing with phosphorus and small negative/positive heats of mixing with Ni. In addition, X4 have even lower X4–X4 bond energies than those of X3, i.e. lower X4–P bond energies. However, X4 have relatively larger atomic radius, which are similar or slightly larger than those of X2, thus high packing density similar or slightly larger than those of X2. Moreover, the solubility of X4 in major
phase Ni$_3$P are negligible. Al can dissolve into Ni for about 7 at.%, which would segregate into minor phase Ni during crystallization. Pd, Ag, In, Sn, Au, Pb, Bi have negligible solubility in Ni, thus forming X4-rich minor phase. Therefore, the combined effect of weak X4–P bonds, large atomic radius ratio, and X4 element segregation may lead to e slightly lower than those of X2.

Then, we discuss element X5 (X5: Cr, Mn, Cu). X5 show small negative heats of mixing with phosphorus (except Cr and Mn) and small negative/positive heats of mixing with Ni. In addition, X5 have lower X5–X5 bond energies close to those of X4, i.e. low X5–P bond energies. Moreover, X5 have atomic radii similar to or slightly lower than that of Ni, which would not contribute to increasing packing density. X5 are probably not able to significantly dissolve into major phase Ni$_3$P due to different electron configuration with Ni, although they show similar atomic radius to Ni. X5 can dissolve into Ni during crystallization, which would segregate into minor phase Ni during crystallization. Therefore, the combined effect of weak X5–P bonds, small atomic radius ratio, and X4 element segregation may lead to e slightly lower than those of X4.

Finally, we discuss element X6 (X6: Zn, Cd). X6 show small negative heats of mixing with phosphorus and small negative/positive heats of mixing with Ni. In addition, X6 have the lowest X6–X6 bond energies, i.e. the lowest X6–P bond energies. Moreover, X6 have atomic radius that are similar or slightly larger than those of X2, thus high packing density similar or slightly larger than those of X2. X6 are probably not significantly
dissolved into major phase Ni$_3$P, similar to X5. Zn can dissolve into Ni during crystallization, which would segregate into minor phase Ni during crystallization. Cd does not significantly dissolve into Ni, which would segregate into Cd-rich minor phase. Therefore, the combined effect of extremely weak X6–P bonds, large atomic radius ratio, and X6 element segregation may lead to $e$ lower than those of X4.

In conclusion, the general trend of retarding crystallization effectiveness $e$ is $X_1 \approx X_2 > X_4 > X_5 \approx X_6 > X_3$. The $e$ also varies inside each catalog. In addition, the classification depends on the selection of cut-off heat of mixing, bond energy and atomic radius ratio, therefore, the classification is not rigid. It is possible that the elements near the both ends of each catalog overlaps, resulting in different sorting of $e$ for specific elements.

This trend is similar to the observed thermal stability of Ni–X–P, shown in Fig 1.5. Moreover, Inoue$^{25}$ also studied the thermal stability of Fe–X–P systems (X: Nb, W, Mo, Al, V, Ti, Cr, Mn, Ni, Co). By alloying a small fraction of X ($\approx 4$ at.%), the retarding crystallization effectiveness $e$ trend is Nb > W > Mo > V $\approx$ Al > Ti > Cr $>$ Mn $>$ Ni $>$ Co. The results are very similar to those of our analyses. This suggests that our proposed criteria are generally valid in metal-metalloid systems that are similar to Ni–P, such as Fe–P, Fe–B, Co–P, Co–B, and probably others.

It can also be seen that there is a maximum crystallization peak temperature $T_P$ at a constant heating rate by alloying a small fraction of a third element X. To further increase the $T_P$, it is desired to co-alloying a
fourth and/or fifth element, which can reach even higher packing density due to large atomic radius difference, produce more complicated element segregation, generate more strong bond breaking.

4.3.2 Technical Aspects

While the criteria suggest what element to select, the practical options for synthesizing the amorphous state determine the actual properties of the alloyed amorphous system. Electroless plating is a bottom-up way to make amorphous alloys atom by atom. This is different from melt-spinning and rapid quenching, which make amorphous alloys from the melt. Therefore, the factors that determine the quality of the amorphous alloys are plating parameters, such as chemical concentrations, the bath stability, pH, bath temperature, etc, other than the GFA, which is usually the concern of melt-spinning and rapid quench. High thermal stability can only be achieved by depositing a high quality amorphous layer with uniformly distributed elements and without formation of metastable phases during tempering. Therefore, optimizing the plating parameters is of vital importance.
5 Conclusion

(1) We have accomplished to deposit tungsten-alloyed amorphous Ni–P by electroless plating, which has properties that are interesting for fundamental science as well as applications. Amorphous Ni–W–P exhibits higher thermal stability than amorphous Ni–P, while keeping paramagnetism in as-plated state and decreases the saturation magnetization after crystallization.

(2) Physical theory has been developed from the following aspects to explain what the effect of tungsten on crystallization behavior:

i. Macroscopic aspect (energetics and kinetics), the presence of tungsten reduces the driving force and increases the activation energy for crystallization.

ii. Microscopic aspect (micro-mechanism), the presence of tungsten reduces free volume (hypothesis) due to large $r_{W}/r_{Ni}$ and $r_{W}/r_{P}$; introduces tungsten atoms diffusion to segregate due to chemical potential difference in different crystalline phases; involves the breaking of all of W–P bonds with high bond energy.
(3) Theoretical criteria of an effective metal X alloying to improve the thermal stability of M–ML (metal–metalloid) amorphous systems has been proposed. The criteria are:

i. Large negative heat of mixing among X, M and ML.

ii. Minimum amorphous free volume by appropriate combination of $r_X$, $r_M$ and $r_{ML}$.

iii. Large chemical potential difference of X in minor than in major crystalline phase.

iv. Large X–ML and X–M bond energy.

The criteria enable straightforward identification of other alloying that will effectively retard crystallization, which has implications for fundamental science and technologies.
6 Proposed Future Work

6.1 Space Group Identification of h-Ni$_3$P by Microdiffraction

h-Ni$_3$P is an important metastable phase formed during crystallization of some Ni–P or Ni–X–P. However, its crystal structure (space group) is unknown until now. The understanding of its crystal structure will help us understand its connection with amorphous atomistic structure, and thus understand the reason of its formation. Once we know the reason of its formation, we could probably be able to find directions to adjust electroless plating parameters to avoid its formation, which will further improve the thermal stability of the amorphous Ni–X–P.

Space groups of unknown phases are usually identified by CBED patterns. The crystal point group can be obtained by careful study of the two-dimensional and three-dimensional features shown in the transmitted as well as diffracted disks. However, many specimens, especially those composed of small crystals, small particles or crystals with large lattice parameters, give relatively poor CBED patterns showing little or no intensity variations within the disks. Therefore, point group identification is impossible in this way. h-Ni$_3$P is just the case. Although h-Ni$_3$P grains
are relatively large (about 5 \( \mu \text{m} \) in length), a lot of small subgrains as well as a high density of Ni nano-particles inside one grain lead to very poor CBED patterns.

Morniroli et al. found that microdiffraction patterns obtained with a small convergent angle electron diffraction can help reveal the Bravais lattice and the presence of glide planes and screw axes of unknown phases.\(^9\)\(^6\) Such information leads to the space group deduction. Although this method requires a very careful tilting to zone axis for small subgrains, it is not entirely impossible. Therefore, microdiffraction technique will be attempted to identify the space group of h-Ni\(_3\)P.
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