Microstructure and Mechanical Properties of Cr, Mo, Fe, Ta Modified Pd–Ni–Cu–P Glassy Alloys Prepared by Copper-Mold Casting

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By incorporating small amounts (0 ≤ 5 at%) of transition metals (TM) of Cr, Mo, Fe and Ta into Pd$_{40}$Ni$_{10}$P$_{20}$ alloy that has been considered to be the best glass former so far, in-situ composites consisting of a glassy phase and nano- and/or micro-sized crystalline particles were prepared by copper-mold casting. The nano- and micro-sized particles identified to be phosphides are homogeneously dispersed in a glassy matrix. The formation of such a characteristic structure is attributed to a primary crystallization reaction with high nucleation rate and limited growth rate in the undercooled Pd$_{40}$Cu$_{30-x}$Ni$_{10}$P$_{20}$TM melt. The TM atoms interact preferentially with the clusters of Pd–Ni–P, one kind of atomic units in the deeply undercooled Pd–Cu–Ni–P liquid, and result in the formation of the TM–Ni–P or TM–Ni–P–Pd clustered units in the undercooled melt, which act as nucleation sites during solidification. With the addition of Cr, Mo, Fe and Ta atoms into Pd$_{40}$Cu$_{30-x}$Ni$_{10}$P$_{20}$ alloy, the first phosphide phases precipitated from these melts are Ni$_{33}$Cr$_{33}$P$_{33}$, MoNiP, Fe$_{33}$Ni$_{33}$P$_{33}$, and (Pd,Ta)NiP, respectively. These phases possess the same hexagonal structure as Fe$_2$P (hP9). The dispersed particles have a volume fraction ranging from 9 to 18% for the alloys investigated. The compressive strength and ductility of these glassy composites are not significantly improved by the dispersion of the nano- and micro-sized particles. These glassy composites deformed by an inhomogeneous shear slip mode and fractured by an adiabatic shear mechanism. The nucleation behavior and the effect of dispersed particles on the deformation and fracture behavior are discussed.

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1. Introduction

It is an important observation that nanoparticles dispersed in glass matrix improve both the strength and ductility of some glassy alloys.1,2) Since a fully glassy material is brittle from an engineering point of view,3,4) this observation is expected to extend this novel material to structural applications. Two methods have been used to produce nanoparticle-dispersed bulk metallic glasses:5) 1) annealing of a cast glassy alloy to an elevated temperature; 2) casting of a molten alloy. Although the first route offers the advantages of being less sensitive to casting conditions and a more uniform microstructure, the metallic glasses exhibit a tendency of embrittlement due to the structural relaxation caused by annealing treatment.6) Moreover, there are some reasons to suppose that annealing treatment cannot produce the finest microstructure.7) Therefore, processing of nano-sized glassy composites by the casting technique has attracted much attention.5,8) We have reported in another paper that nanoparticle-dispersed bulk metallic glasses in Cr-added Pd$_{40}$Cu$_{30-x}$Ni$_{10}$P$_{20}$Cr$_{x}$ alloys can be formed directly by copper-mold casting.9) The nanoscale Cr$_{33}$Ni$_{33}$P$_{33}$ (Fe$_2$P, hP9) particles, which were homogeneously distributed in the glassy matrix, precipitated from the melt during solidification. It has been speculated that,9) since the heat of mixing of Cr–Cu atom pairs is positive, the Cr atoms interact preferentially with the cluster of Pd–Ni–P rather than with that of Pd–Cu–P, which are the two kinds of clusters composed in supercooled liquid of Pd$_{40}$Cu$_{30}$Ni$_{10}$P$_{20}$.10) As a result, the Cr–Ni–P or Cr–Ni–P–Pd clustered units are formed in the undercooled melt and act as nucleation sites during solidification. It is interesting to know whether the speculation is operative in the Pd–Cu–Ni–P alloys modified by other alloying elements, whose heat of mixing with Cu is also positive. Further more, this knowledge is of technical and scientific importance. From the technical point of view, the introduction of homogenous nucleation sites in an undercooled melt is crucial for producing nanoscale glassy composites by the conventional casting technique. From scientific point of view, the influence of the incorporated atoms on the thermal and structural stability of the supercooled liquid is important for the understanding of the physical nature of glass-forming ability.

Many elements in the periodic table possess positive heat of mixing with Cu atoms and negative values with other elements in the Pd–Cu–Ni–P alloy. But some of them, e.g., Ti, Zr, Hf, V, Nb, and Al etc., react with B$_2$O$_3$ in the fluxing treatment process. Therefore, in this study, besides Cr, three other transition metals, i.e. Fe, Mo, and Ta were selected as additional alloying elements. In this paper, we have investigated the solidification behavior, microstructure and mechanical properties of the TM-added Pd$_{40}$Cu$_{30-x}$Ni$_{10}$P$_{20}$TM alloys prepared by copper-mold casting. The effect of the dispersed particles on the deformation and fracture behaviors is also discussed.

2. Experimental Procedure

Alloys with compositions of Pd$_{40}$Cu$_{30-x}$Ni$_{10}$P$_{20}$TM (TM = Cr, Mo, Fe, Ta; x = 0–5 at%) were investigated in the work. The alloy ingots were first prepared by arc melting the mixtures of pure Pd, Ni, Cu, and TM metals and pre-alloyed Pd–P ingots at selected compositions in an argon atmosphere. The ingots were subsequently flux treated with B$_2$O$_3$ by the same arc melting method. Finally, from these fluxed ingots, cylindrical rods of 3 mm in diameter were prepared by injection casting of the molten alloys into copper mold with a cylindrical cavity. Alloy ribbons were also prepared by a melt-spinning method. The cast structure was examined by X-ray diffraction (XRD), transmission electron
microscopy (TEM) and scanning electron microscopy (SEM). The thermal properties of these alloys were examined by differential scanning calorimetry (DSC). The hardness was measured using a Vickers hardness tester. The compressive strength was evaluated by compression test using specimens which were cut from the cast cylindrical rods by 6 mm in length. The cut surfaces were polished with SiC paper. The specimens were compressed between hard BN plates in an Instron machine. Compression tests were carried out at an initial strain rate of $4 \times 10^{-4}$ s$^{-1}$ at room temperature. Since the fracture data were inevitably scattered, at least five samples were tested for each alloy. Fracture surface was examined using an SEM.

3. Results

3.1 Cast structure

It is confirmed by XRD analyses that the melt-spun ribbons of the studied alloys consist of a fully glassy phase. However, the cast 3 mm diameter-rod with the corresponding composition is composed of a glassy phase containing one or two kinds of crystalline phases. Figures 1(a) to (d) show the cast structures of Pd$_{40}$Cu$_{30}$Ni$_{10}$P$_{20}$TM$_x$ containing Cr (1 at%), Mo (5 at%), Fe (3 at%) and Ta (5 at%), respectively. Figures 1(a), (c) and (d) are backscattered electron images and (b) is a secondary electron micrograph. The constituent phases and crystalline structures, which were identified by XRD, are summarized in Table 1. Also included are the magnitude orders of the particle sizes, which were estimated from the

![Fig. 1 Cast structures of Pd$_{40}$Cu$_{30}$Ni$_{10}$P$_{20}$TM$_x$ (TM = Cr, Mo, Fe and Ta) alloys. (a) 1 at%Cr; (b) 5 at%Mo; (c) 3 at%Fe; (d) 5 at%Ta.](image)

**Table 1** Characteristics of compounds formed in Pd$_{40}$Cu$_{30}$Ni$_{10}$P$_{20}$TM$_x$ glassy alloys (TM = Cr, Mo, Fe and Ta, $x = 1, 3,$ and 5).

<table>
<thead>
<tr>
<th>Alloying elements</th>
<th>at%</th>
<th>Compounds</th>
<th>Crystal Structure</th>
<th>Order of size</th>
<th>Volume (%)</th>
</tr>
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<tbody>
<tr>
<td>Cr</td>
<td>1</td>
<td>Cr$<em>{133}$Ni$</em>{133}$P$_{14}$</td>
<td>Fe$_2$P, hP9</td>
<td>nano</td>
<td>9–13</td>
</tr>
<tr>
<td></td>
<td>3–5</td>
<td>Cr$<em>{133}$Ni$</em>{133}$P$_{14}$</td>
<td>Fe$_2$P, hP9</td>
<td>summicro + micro</td>
<td>13–16</td>
</tr>
<tr>
<td>Mo</td>
<td>3</td>
<td>MoNiP</td>
<td>Fe$_2$P, hP9</td>
<td>submicro</td>
<td>9–12</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>MoNiP + Mo$_2$P</td>
<td>Fe$<em>2$P, hP9 + SV$</em>{32}$, hP32</td>
<td>nano + micro</td>
<td>15–18</td>
</tr>
<tr>
<td>Fe</td>
<td>3–5</td>
<td>Fe$<em>{133}$Ni$</em>{133}$P$_{14}$</td>
<td>Fe$_2$P, hP9</td>
<td>submicro + micro</td>
<td>12–18</td>
</tr>
<tr>
<td>Ta</td>
<td>1</td>
<td>(Pd,Ta)NiP</td>
<td>Fe$_2$P, hP9</td>
<td>nano</td>
<td>9–12</td>
</tr>
<tr>
<td></td>
<td>3–5</td>
<td>(Pd,Ta)NiP + TaNiP</td>
<td>Fe$_2$P, hP9 + Co$_2$Si, oP12</td>
<td>nano + micro</td>
<td>12–15</td>
</tr>
</tbody>
</table>
microstructure observations. To simplify the description, the particle sizes are categorized into the following three groups: 1) nano-scale; 2) submicro-scale; 3) micro-scale. In the nano-scale group, the particles have a nearly equiaxial-faced shape with an average size of about 500 nm and an average interspacing of about 400 nm. Such structures are observed in the alloys with low TM contents, ordinarily less than 3 at% TM. In the sub-micro group, the particles always show small dendritic shape with an average particle size of about 1 \( \mu m \) and an average interparticle spacing of about 1 \( \mu m \). Not that in the areas between the submicro-scale particles always exist nano-scale particles. Such structures are observed in the alloys with 3–5 at% Cr and Fe. The micro-scale structures are observed in the 5 at% Mo and 3–5 at% Ta alloys. The particles have shapes of large blocks or flat plates. Nano-scale particles are observed in the areas between the micro-scale particles.

It is clear from Table 1 that the crystalline phase is \( \text{Ni}_{33}\text{Cr}_{33}\text{P}_{34} \) in the Cr-added alloys, \( \text{Fe}_{33}\text{Ni}_{33}\text{P}_{34} \) in the Fe-added alloys. At Mo \( \leq 3 \) at% and Ta \( \leq 1 \) at%, the crystalline phases are \( \text{MoNiP} \) and \( (\text{Pd,Ta})\text{NiP} \) in the Mo-added alloys and Ta-added alloys, respectively. All these phases have the same hexagonal crystal structure, \( \text{Fe}_2\text{P} \) (\( \text{hP9} \)). Their particle sizes are of nano and/or sub-micro order, which increase with increasing TM contents. In contrast, the number of particles tends to decrease with increasing TM contents.

At Mo content exceeding 3 at% and Ta content exceeding 1 at%, two kinds of crystalline phases crystallized from each melt. In the 5 at% Mo alloy (Fig. 1(b)) the small particles are \( \text{MoNiP} \) (\( \text{Fe}_2\text{P} \), \( \text{hP9} \)), while the large dark particles are \( \text{Mo}_3\text{P} \) (\( \text{SV}_3 \), \( \text{Ir32} \)) with an average composition of \( \text{Mo}_{70}\text{P}_{20}\text{Si}_{5}\text{Cu}_{5} \). In the 5 at% Ta alloys (Fig. 1(d)) the small particles are \( (\text{Pd,Ta})\text{NiP} \) (\( \text{Fe}_2\text{P} \), \( \text{hP9} \)), while the large bright particles is \( \text{TaNiP} \) (\( \text{CO}_2\text{Si} \), \( \text{oP12} \)) with an average composition of \( \text{T}_{34}\text{Ni}_{31}\text{P}_{32.5}\text{P}_{0.5} \). The particle sizes of \( \text{Mo}_3\text{P} \) (\( \text{SV}_3 \), \( \text{Ir32} \)) and \( \text{TaNiP} \) (\( \text{CO}_2\text{Si} \), \( \text{oP12} \)) phases are several micrometers.

### 3.2 Thermal stability of supercooled liquid

In order to investigate the influence of alloying on the thermal stability of supercooled liquid, the melt-spun ribbons with a fully glassy phase were used in the DSC experiments. Figures 2(a) to (d) show the DSC curves of the melt-spun ribbons. By increasing the TM content in the \( \text{Pd}_{40}\text{Cu}_{30-\ell}\text{Ni}_{10}\text{P}_{20}\text{TM}_{\ell} \) alloys, the crystallization reaction changes from single stage mode to multiple stage mode. Cr and Ta significantly decrease the thermal stability by a gradual increase in the glass transition temperature, \( T_g \), and a rapid decrease in the crystallization temperature, \( T_x \). On the other hand, the supercooled liquid region (\( \Delta T_s = T_s - T_x \)) slightly increases with 1 at% Mo or 1 at% Fe addition, and then decreases with increasing Mo or Fe content.

The endothermic peaks due to melting are seen for all the alloys and the melting reaction appears to occur through multiple stages (Fig. 2). The \( T_s \) denotes the onset temperature of the endothermic peak, which is about 800 K in the Cr, Mo and Ta added alloys and remains unchanged within the content range up to 5 at%. It is known that an invariant eutectic reaction of \( L \rightarrow \text{Cu}_3\text{Pd} + \text{Ni}_2\text{Pd}_2 + \text{Cu}_3\text{Pd}_5 + \text{Cu}_3\text{Pd}_5 \) quaternary phosphide occurs at this temperature in \( \text{Pd}_{40}\text{Cu}_{30-\ell}\text{Ni}_{10}\text{P}_{20} \). This result suggests that the eutectic reaction remains unchanged by the addition of Cr, Mo or Ta.

![Fig. 2 DSC curves of Pd\textsubscript{40}Cu\textsubscript{30-\ell}Ni\textsubscript{10}P\textsubscript{20}TM\textsubscript{\ell} (TM = Cr, Mo, Fe and Ta) melt-spun ribbons. (a) Cr; (b) Mo; (c) Fe and (d) Ta.](image-url)
The $T_c$ temperature increases with increasing Fe content when Fe > 1 at%, suggesting that the Fe added alloys are off the invariant eutectic reaction region. It is evident that the studied alloys, except the Fe added alloys (Fe > 1 at%), are located in an invariant eutectic reaction region.

The crystallization behavior for some ribbon samples was also investigated. The precipitated phase was identified as $\text{Cr}_{33}\text{Ni}_{33}\text{P}_{34}$ (Fe$_2$P, $hP9$) in the 1 at%Cr-added melt-spun ribbon, which was annealed at the temperature near the first crystallization peak. This phase is the same as that in the rapidly solidified alloy.

### 3.3 Mechanical properties

Figure 3 shows the change of the compressive fracture strength ($\sigma_f$) as a function of TM content. This figure reveals a decrease tendency of the $\sigma_f$ with TM content. The bars in the figure denote the scattered ranges of the experimental data, which also increase with increasing TM content.

Only elastic deformation is observed before fracture for almost all the samples. A group of nominal stress–strain curves are plotted in Fig. 4, showing the compressive behavior of the Cr added alloys. As is seen, some samples with higher alloying contents exhibit early fracture.

### 3.4 Fractographic observation

The fracture features of a fully glassy alloy in Pd–Cu–Ni–P system have been described in another paper. In this study, a detailed SEM fractographic analysis was carried out to examine the fracture mode for the particle dispersed glassy composites.

Except for a few samples with high Cr or Ta contents, which were fragmented into many pieces under compression, the studied samples fractured into two large and several small segments. The major crack surface is easily recognized for the fractured segment which lies at an angle of 40–60 degrees to the loading axis. Figure 5 shows an example of the fractured surface of the 5 at%Fe alloy. The dominant fractographic feature on the major fracture surface is vein-like or river-like patterns, similar to that of the fully glassy alloys. Figure 6(a) shows a typical vein-like structure of the 5 at%Cr alloy. Note that the vein pattern is not smooth and some knots appear along the vein. This knotted vein pattern is commonly observed for the alloys containing sub-

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Fig. 3 Changes of compressive strength of Pd$_{40}$Cu$_{30}$Ni$_{10}$P$_{20}$TM$_x$ (TM = Cr, Mo, Fe and Ta) alloys as a function of TM content.

Fig. 4 Compressive stress–strain curves of Pd$_{40}$Cu$_{30}$Ni$_{10}$P$_{20}$Cr$_x$ ($x = 0, 1, 3$ and $5$) alloys.

Fig. 5 SEM images showing the side and top appearance of the fractured Pd$_{40}$Cu$_{30}$Ni$_{10}$P$_{20}$Fe$_1$ glassy alloy.
micro particles, but is rare in the nano-sized alloys. As is seen in Fig. 6(b), the groove morphology is often observed in these composites. Note that at the end of the groove a particle is always observed, indicating that the groove is formed by the particle sliding. Micro-crack morphology is another important fractographic feature for these glassy composites. Figures 6(c) and (d) show SEM images of the 1 at%Cr and 5%Mo alloys. Figure 6(c) is typical microcrack morphology on the major fracture surface, including submicron particles, while Fig. 6(d) is typical microcrack morphology with the cracks in microscale particles (Mo3P).

As is observed in the fully glassy Pd–Cu–Ni–P alloy,10 a number of ‘liquid droplets’ were also observed on the fracture surface of these glassy composites, indicative of adiabatic heating at the final fracture stage. Figure 7 shows some SEM images of the remelting morphology. It is clear in

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Fig. 6  SEM images of fracture surface of glassy composites showing typical (a) knotted-vein pattern (5 at%Cr), (b) groove morphology (5 at%Cr), (c) microcrack morphology (1 at%Cr) and (d) cracks in large particles (5 at%Mo).

Fig. 7  ‘Remelting droplets’ morphologies taken from Pd40Cu29Ni10P20Fe1 alloy, showing (a) the fluid flow on the ‘true’ fracture surface and (b) a filament drawn from a remelted droplet.
Fig. 7(a) that the melt flows on the fractured surface and covers the true fracture morphology. A filament drawn from a remelted droplet is shown in Fig. 7(b), indicating that the local temperature is over the \( T_g \) temperature.

4. Discussion

4.1 Solidification behavior

4.1.1 Solidification mode

A glass former under deeply undercooled condition may be solidified (or crystallized) to nano-structure via primary,\(^5,\,7,\,12\) polymorphous\(^\text{13}\) or spinodal reaction.\(^\text{14}\) In the present study, the precipitated compounds are the TM enriched phosphide, indicating that a solute partitioning process occurred during solidification. Therefore, the present solidification mode cannot be interpreted by a polymorphous reaction. On the other hand, it is known that in some cases, a eutectic melt would undergo liquid spinodal decomposition, becoming a metastable liquid network of wavelength \( \lambda \). Upon crystallization, nanostructures have been formed in those of \( \lambda < 100 \text{ nm} \).\(^\text{14}\) The present alloys, except for the Fe \( \geq 3 \) at% alloys, are located near a eutectic point. Although no specific evidence of spinodal-network morphology is obtained in the cross section of the 3 mm-diameter cast rods, we could not simply rule out this possibility. To clarify this, the cast structure in a wedge sample was investigated. The wedge sample was prepared from Pd\(_{30}\)Cu\(_{30}\)Ni\(_{10}\)P\(_{20}\) by casting the molten alloy into a copper mold with a wedge cavity. Since the cooling rate along the length of the wedge sample is different and changes in a wider range than that in the 3 mm-diameter cylindrical sample, the spinodal network morphology should be observed in some areas where the undercooling satisfies a spinodal reaction if it really exists in this alloy system. Not any evidence of spinodal networks was observed over the lengthwise cross section of the wedge sample, suggesting that the crystallization is not caused by a spinodal mechanism. Therefore, it is reasonable to conclude that the crystallization occurs via a primary precipitation reaction.

4.1.2 The critical cooling rate \( R_c \) and nucleation frequency of TM added alloys

The \( R_c \) of the TM-free Pd\(_{30}\)Cu\(_{30}\)Ni\(_{10}\)P\(_{20}\) alloy has been reported to be about 0.1 K/s,\(^\text{15,\,16}\) The cooling rate under the present copper-mold casting condition is conservatively estimated to be 100 K/s. Even though this value is three orders of magnitude higher than the \( R_c \) of the TM-free Pd\(_{30}\)Cu\(_{30}\)Ni\(_{10}\)P\(_{20}\) alloy, the crystallized structures shown in Fig. 3 clearly indicate that this cooling rate is still insufficient to suppress crystallization in the undercooled melt. Obviously, the \( R_c \) of the Pd\(_{30}\)Cu\(_{30}\)Ni\(_{10}\)P\(_{20}\)TM\(_x\) alloys is dramatically increased by the additions of small amounts of TM. In other words, the glass-forming ability is remarkably decreased by the addition of small amounts of TM. This is consistent with the DSC results that the thermal stability (measured by the \( \Delta T_f \)) of supercooled liquid is dramatically degraded by the TM addition.

The exceptionally small \( R_c \) of the TM-free Pd\(_{30}\)Cu\(_{30}\)Ni\(_{10}\)P\(_{20}\) is attributed to the extremely low nucleation rate of a crystalline phase.\(^\text{15-\,19}\) It is suggested that under homogenous nucleation condition, the primary phase precipitated from the deeply undercooled melt is Pd\(_{32}\)P\(_2\), which has a rhombohedral structure with large lattice parameters \( (a = 0.711 \text{ nm} \ and \ c = 1.709 \text{ nm}) \).\(^\text{19}\) The formation of such a phase requires a significant change in the local atomic structure, which contributes to the high glass-forming ability of the TM-free Pd–Cu–Ni–P alloy.

The dramatic increase in \( R_c \) for the TM-added alloys can only be understood on the basis of the effect of the TM elements on the atomic structure of the undercooled liquid as well as the nucleation mechanism during solidification. The undercooled melt of the TM-free Pd\(_{30}\)Cu\(_{30}\)Ni\(_{10}\)P\(_{20}\) is composed of two clustered units of Pd–Ni–P and Pd–Cu–P.\(^\text{3}\) We have speculated that,\(^\text{3}\) in the Cr-added Pd\(_{30}\)Cu\(_{30}\)Ni\(_{10}\)P\(_{20}\) alloys, since the mixing heat of Cr–Cu atom-pair is positive, the Cr atoms interact preferably with the cluster of Pd–Ni–P rather than with Pd–Cu–P, and the result is the formation of the Cr–Ni–P or Cr–Ni–P–Pd clustered units in the undercooled melt. These clustered units act as nucleation sites during further solidification. The present study offers more evidence to support this speculation. Fe, Mo and Ta also possess positive mixing heats with Cu and negative values with other elements in the Pd–Cu–Ni–P system. The favored formation of TM–Ni–P or TM–Ni–P–Pd clustered units results in a high nucleation rate during solidification, which contributes to the dramatic decrease in glass-forming ability for the Pd\(_{30}\)Cu\(_{30}\)Ni\(_{10}\)P\(_{20}\)TM\(_x\) alloys.

This speculation is also supported, even though indirectly, from the cast structures of the Pd\(_{30}\)Cu\(_{30}\)Ni\(_{10}\)P\(_{20}\) alloys. Since the glass-forming ability decreases with a deviation of the composition from the eutectic point (near Pd\(_{40}\)Cu\(_{30}\)Ni\(_{10}\)P\(_{20}\)),\(^\text{18}\) a crystallized cast structure must be obtained along the composition line of Pd\(_{30}\)Cu\(_{30}\)Ni\(_{10}\)P\(_{20}\) (\( x = 1, \, 1.5, \, 2, \ldots \)). Figure 8 shows the cast microstructure of the Pd\(_{32}\)Cu\(_{30}\)Ni\(_{17}\)P\(_{20}\) (\( x = 7.5 \)). As can be seen, a few dendritic particles, which are identified as CuPd, sparsely dispersed in a glassy matrix, indicating that the decrease in glass-forming ability is not due to the formation of homogenously dispersed nucleation site but different from that in the TM-doped Pd–Cu–Ni–P alloys.

In addition, the nucleation rate is thought to be controlled by the number density of Pd–Ni–P clusters in melt. This
presumption is supported from the fact that the particle number is independent of the TM content and increases with increasing Ni and P contents. By the formation of TM-rich clusters, on the other hand, TM-depleted areas around TM-rich clusters are also formed, which contributes to the limited growth rate of the nuclei.

From the above discussion, the major factors that favorably affect the formation of ultra fine structure in the Pd_{10}Cu_{90–4}Ni_{10}P_{20}TM_{x} alloys can be summarized as follows: 1) the unique atomic structure of Pd–Cu–Ni–P supercooled liquid, which is extremely thermally stable in deeply undercooled liquid; 2) special alloying elements, which can destroy partially the original atomic structure and result in the formation of new atomic clusters; 3) limited growth rate of nuclei; 4) high glass-forming ability of the remaining liquid.

It is clear that the atomic configuration (short-range order) of the undercooled liquid directly affects the nucleation behavior, and consequently the glass-forming ability. This of the undercooled liquid directly affects the nucleation behavior, and consequently the glass-forming ability. This implies that the formation mechanism of the undercooled liquid is under investigation. Some preliminary results show that the first crystalline phase lies above that of the glass phase. If the two phases are loaded to the same tensile or compressive stress, the tensile (or compressive) stress–strain behavior for a multi-structure containing crystalline and glassy phases, these two phases must cooperate with each other in the boundary region when the tensile or compressive stress is applied to the glassy phase.

4.1.3 Solidification and devitrification

The present cast structure is formed under a rather high cooling rate by copper-mold casting. In other words, the solidification takes place in a deeply undercooled liquid. This solidification process may somewhat differ from that of the devitrification reaction, because the cooling history must be considered in the latter process. The detailed devitrification behavior for the TM-added melt-spun ribbons is under investigation. Some preliminary results show that the first precipitated phase in the 1 at% Cr-added ribbon, which was annealed at a temperature near the first crystallization peak, is a Cr_{33}Ni_{53}P_{34} (Fe_{33}P_{34}, hP9) phase, the same as that of the cast alloy. This implies that the formation mechanism of the crystallized structures during casting and devitrification is similar. This can be understood on the basis of the concept that the glass is a ‘freezing’ of deeply undercooled liquid and the atomic structure of this deeply undercooled liquid is frozen in the glass state.

4.2 Mechanical properties of glassy composites

4.2.1 Role of the dispersed particles

Because there is no micro-scale structures such as grain boundaries and specific phase boundaries, mechanical properties of glassy alloys are dominated by the atomic-scale structures, such as free volumes, clusters and chemical composition, etc. Theoretically it is possible to further improve the mechanical properties of glassy alloys by manipulating the structure variations at micro-scale to achieve various strengthening mechanisms. Numerous important and interesting experiments have been reported in this aspect. For example, by in-situ formation or ex-situ addition of dispersed nano- and micro-particles in a glassy matrix, Inoue et al. successfully improved the fracture strength and ductility for Al-, Mg-, Zr- and Cu-based glassy alloys.

However, the present results clearly show that the strength and ductility of the Pd–Cu–Ni–P–TM glasses cannot be improved by the dispersion of nano-, sub-micro- and micro-precipitates. It means that the strengthening mechanisms that are effective in fcc-Al/Al-based, hcp-Mg/Mg-based, I-phase/Zr-based, Zr_{2}(Cu, Pd)/Zr-based, W/Zr-based, ZrC/Zr-based and ZrC/Cu-based glassy systems do not effectively work in the present phosphide/Pd-based glassy system.

To further understand the present results, we briefly discuss the factors affecting the strength and ductility of glassy composites. The most important one is the particles per se, including their geometry, crystallinity and mechanical properties. The nonlinear increase in bending strength for crystal-cluster/Zr-based glasses well demonstrates the ‘quantum size effect’. This phenomenon cannot be explained by the precipitation hardening mechanisms (particle looping and particle cutting) operating in conventional crystalline materials, because there is no dislocation in a glass matrix. Combining the deformation and fracture mechanisms of a glassy phase, Inoue suggested that when the particles are small enough that they can be considered as free defect and comparable in dimension with the width of shear bands, the separated particles can act as an effective barrier to the local shear deformation, which consequently increases the strength of the material. Moreover, the residual compressive stress in the glassy region close to the clustered particles may also contribute to the strength increase. Note that in this ultra fine particle case, the effect of mechanical nature of this particles on the strength and ductility of glassy matrix is still unclear at this point.

As the particle size increases, though in some cases the particle size is still in the order of ‘nano-scale’, the crystal structure and the mechanical nature of the particle in bulk state become important. For example, the precipitation of brittle intermetallic MgCu in Mg_{55}Cu_{22}Y_{10} glass causes a decrease in the ductility of the glass matrix. On the other hand, the precipitation of a ductile solid solution of fcc-Mg in Mg_{50}Cu_{10}Y_{10} and hcp-Mg in Mg_{83}Zn_{12}La_{5} results in an improvement of ductility. This phenomenon may be supported by reference to Fig. 9. This figure schematically shows the tensile (or compressive) stress–strain behavior for a crystalline and a glassy single phase. Here, the Young’s modulus of the crystalline phase is assumed to be higher than that of the glass phase. Thus the stress–strain plot of the crystalline phase lies above that of the glass phase. If the two phases are loaded to the same tensile or compressive stress, σ_{i}, a larger strain will be achieved in the glass phase (σ_{glass} > σ_{crystal}); on the other hand, if the two phases are deformed to the same strain, ε_{i}, a higher stress will be needed in the crystalline phase (σ_{crystal} > σ_{glass}). In a multi-structure containing crystalline and glassy phases, these two phases must cooperate with each other in the boundary region when
the structure is subjected to deformation. This will lead to stress concentration in this region. The value of stress concentration is mainly determined by the bonding strength of the two phases. Qualitatively, the stress concentration may cause a plastic deformation in a ductile crystalline phase or a crack in a brittle crystalline phase when its value exceeds the yield stress of the crystalline phase. It may also result in an interface crack when its value exceeds the bonding strength at the interface or in the particles are easily formed due to excessive free volume.

In a sense, increasing the particle volume fraction gives rise to an increase in the density of stress concentration sites. It has been reported that the Young’s moduli of fcc-Al/Al-based and ZrC/Zr-based composites increase linearly with particle volume fraction in a large fraction region, whereas the fracture strength increases linearly only in a smaller volume fraction region. This indirectly shows the influence of stress concentration because the fracture strength is more sensitive to stress concentration than Young’s modulus.

In the present case, the average particle size is larger than 500 nm, beyond the conventional nano-scale. The phosphide phases have complex crystal structures and are brittle in nature. For instance, the hardness of Cr$_{33}$Ni$_{33}$P$_{34}$ is about 8.85 GPa, much larger than that of the glassy matrix (about 5.0 GPa), indicating a significant difference in Young’s moduli between the two phases. It is expected that cracks at the interface or in the particles are easily formed due to a smaller elastic deformation durability for the hard particles than the glassy matrix. The microcrack morphologies shown in Figs. 6(c) and (d) are consistent with the present discussion. The ‘strain-induced softening’ layer may also be formed in some boundary areas subjected to tensile stress and contribute to the fracture process.

4.2.2 Role of the glass phase

The inherent nature of glassy phase is the other important factor affecting the mechanical properties of a glassy composite, which includes the composition (atomic bonding strength), atomic configuration (short range order) as well as free volume, etc. For example, with a constant volume fraction of fcc-Al nanoparticles in Al$_{88}$Y$_{12}$-Ni$_{x}$ glassy alloys, the composition dependence of $\sigma_f$ and $E$ is attributed to the bonding force among the constituent atoms in the glassy matrix rather than the magnitude of the lattice misfit and the strength of the fcc-Al phase itself. The other interesting example is that the optimum particle volume fraction leading to the maximum value of $\sigma_f$ in Zr-based bulk glassy alloys is considerably lower than that for the melt-spun ribbons. This is attributed to the introduction of a large amount of free volumes in melt-spun ribbons than in a water-quenched bulk sample. Excessive free volumes will, on the other hand, decrease the Young’s modulus of the glassy matrix and the bonding strength, leading to a decrease in the degree of stress concentration.

The fractographic observations in this study clearly indicate that the major deformation and fracture modes of the present glassy composites are the same as those of the fully glassy Pd–Ni–Cu–P alloy. In other words, the deformation and fracture behavior in these TM-added glassy composites are controlled by the glassy phase. We have reported that a fully glassy alloy in Pd–Ni–Cu–P system deforms via extremely localized shear sliding and fractures via catastrophic adiabatic shear. The deformation is accompanied by a large adiabatic heating, leading to a temperature rise at least above glass transition temperature within the shear band at the final fracture stage. Note that the increase of temperature begins after onset of yielding. It is expected that a region around the shear band is heated to some extent. The viscosity of the material in this region will be decreased due to the temperature rise. Although the width of shear band is suggested to be very narrow, i.e., about 20–30 nm, the region affected by the adiabatic heating may be much wider than the shear band per se. The groove morphology (Fig. 6(b)) and the knotted vein pattern (Fig. 6(a)) strongly indicate that the thickness of the softened layer caused by adiabatic heating is much larger than the diameter of the particles, which makes the particles unable to arrest the propagation of the shear bands, consequently improving the ductility. Although the adiabatic heating is more likely a dynamic process accompanying the localized plastic deformation of the glass phase, a large volume of the remelted material observed in Pd–Ni–Cu–P glass (see Fig. 7 and Ref. 10), which is seldom observed in other glassy systems, suggests that the adiabatic heating reflects some inherent nature of the glass phase itself. More attention should be given for the adiabatic heating effect when a hardening mechanism of glass phase is considered.

Finally, it should be noted that the concept of ‘ductile phase toughening brittle phase’ has been successfully applied in the preparation of intermetallic and ceramic materials with high strength and high toughness. In that case, the ductile particles embedded in a brittle matrix improve the toughness by stopping the propagation of cracks in brittle matrix. Recently, Hays et al. have shown that in-situ formed large bcc β-phase dendrites in a Zr-based glassy alloy greatly improve the ductility and toughness of the glassy alloy, suggesting that this concept may also be applied to glassy alloys.
5. Summary

By doping the best glass former of Pd$_{50}$Cu$_{30}$Ni$_{10}$P$_{20}$ alloy with small amounts (≤5 at%) of transition metals of Cr, Mo, Fe and Ta, in-situ composites of Pd–Ni–Cu–P glass that contain nano- and/or micro-particles were prepared by the copper-mold casting method. The nano- and micro-sized phosphide particles, homogeneously dispersed in glass matrix, were formed from the melt during solidification. The nano-sized phosphide phases are identified as Ni$_{33}$Cr$_{33}$P$_{34}$, MoNiP, Fe$_{33}$Ni$_{33}$P$_{34}$ and (Pd, Ta)NiP in Cr (0.5 < Cr ≤ 5 at%), Mo (1 < Mo ≤ 3 at%), Fe (≤5 at%) and Ta (1 at%) added alloys, respectively. These phosphide phases have hexagonal structure as Fe$_5$P (hP9). In the 5 at% Mo- and 3 at% Ta-added alloys, micro-sized Mo$_3$P with a structure of SV$_3$ (Ih32) and TaNiP with a structure of Co$_2$Si (oP12) were identified. The largest volume fraction of particles was estimated to be approximately 18% in the case of 5 at% alloying element.

The solidification behavior during casting was discussed in terms of crystallization mode and nucleation mechanism. Four factors are considered to affect the formation of the ultra fine structure in the TM-doped Pd–Cu–Ni–P alloys: 1) the unique atomic structure of Pd–Cu–Ni–P supercooled liquid, which is extremely thermally stable in the deeply undercooled liquid; 2) specific alloying elements, which can destroy partially the original atomic structure and lead to the construction of new atomic clusters; 3) limited growth rate of nuclei due to sluggish atomic diffusion, and 4) high GFA of the remaining liquid. On the basis of an in depth understanding of the relationship between the crystal and the atomic-structure of supercooled liquid, a completely new material with controlled grain size and special crystal-orientation distribution may be synthesized.

The compressive strength of these glassy composites is not apparently improved by the dispersion of the nano- and micro-sized phosphide particles due to the brittle nature of the phosphide. These glassy composites exhibit relatively large elastic strain and a negligible apparent plastic strain due to extremely inhomogeneous deformation. These glassy composites failed adiabatically as observed in the single glassy phase alloys.

In addition to some of the factors, such as particle size, volume fraction and mechanical nature of the particles and glass phases, etc., which are important for the mechanical properties of glassy composites, the stress concentration resulted from particle dispersion and the adiabatic heating tendency of the glass phase are also two crucial factors affecting the ductility and strength of the glassy composites.

REFERENCES