

Plastically deformable Cu–Zr intermetallics

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Two stoichiometric Cu–Zr phases, namely B2 CuZr and CuZr₂, are capable of undergoing significant plastic deformation in compression combined with work-hardening. While the former shows transformation-induced plasticity, there is no phase change during deformation of CuZr₂. Addition of Al or Ti has a strong influence on the characteristics of the deformation behaviour of B2 CuZr. These insights could prove useful for understanding the mechanical properties of related bulk metallic glasses (BMGs) and could help synthesize new BMG matrix composites.

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Intermetallic compounds are interesting candidates for structural applications as they generally exhibit high strength, which does not deteriorate even at increased temperatures [1,2]. Yet the high strength comes at the expense of plastic deformability, and the intrinsic brittleness of many intermetallics is the biggest obstruction for their use in structural parts and sometimes even prevents them from being fabricated into components [1–3]. The intrinsic brittleness of intermetallic compounds traces back to the complex crystal structure and the constraint on dislocation movement this brings. The von Mises (or Taylor) criterion states that at least five independent slip systems are necessary to deform a polycrystal homogeneously [2,3]. The complexity of the often comparatively large unit cells of intermetallics results in a low symmetry and a severely limited number of slip systems, which does not allow for cross-slip of dislocations. This in turn hinders the multiplication of dislocations and, therefore, plastic deformability of intermetallic phases. Furthermore, the large unit cell produces large Burgers vectors and large Peierls stresses, which again aggravate dislocation generation and movement [1–3]. Finally, the grain boundaries often show weak cohesion, especially as harmful impurities often tend to segregate at them, and hence fracture occurs along them (intergranular fracture) [1–3].

As opposed to their crystalline counterparts, monolithic bulk metallic glasses (BMGs) are known to be only

capable of accommodating plastic strain in a highly localized manner by generation of shear bands [4]. The already deformed regions are left to be more prone to further deformation and the outcome is that only a few shear bands form till fracture sets in [5]. This shear softening severely limits the macroscopic plasticity of BMGs. In this respect they are rather similar to intermetallics despite the differences in the structures and in the deformation mechanisms.

A remarkable exception form BMGs derived from equiatomic Cu₅₀Zr₅₀, which exhibit yielding and plastic deformation prior to failure [6,7]. So far, the mechanical properties of Cu–Zr BMGs have never been linked to the deformation behaviour of the crystalline phases in their direct vicinity. In this work we determine the mechanical properties of the intermetallic phases, which form in the vicinity of the equiatomic alloy Cu₅₀Zr₅₀ and the results appear to reveal parallels to the deformation behaviour of the respective Cu–Zr BMGs.

Three intermetallic compounds are of interest here, viz. Cu₁₀Zr₇, CuZr₂ and B2 CuZr. The B2 CuZr phase (Pm-3m) is stable only at temperatures above 988 K and decomposes into Cu₁₀Zr₇ (C2ca) and CuZr₂ (I4/mmm) if the system is given the time to equilibrate [8]. As described in Ref. [9] the B2 phase can be stabilized by exploiting the shape memory effect and in doing so we focus on the influence third alloying elements have on the deformation behaviour of this phase.

Cu_{47.5}Zr_{47.5}Al₅, Cu₅₀Zr_{50-x}Ti_x (0 ≤ x ≤ 7.5) and CuZr₂ pre-alloys were synthesized by arc-melting the

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constituting elements (purity of 99.99% or higher) under protective Ar atmosphere. Long rods (70 mm) with a diameter of 2 mm were produced via suction casting. The CuZr_2 rod was annealed at a temperature of 923 K and subsequently cooled in an Ar flow. The $\text{Cu}_{47.5}\text{Zr}_{47.5}\text{Al}_5$ rod was annealed for 16 h at 1073 K in Ar atmosphere and then quenched to room temperature in an Ar flow within approximately 2 min. The rod was consecutively thermally cycled in a Netzsch DIL 402C dilatometer between 193 K and 673 K at a heating rate of 5 K min^{-1} . For the compression tests, an Instron 5869 was used with a constant strain rate of $1 \times 10^{-4} \text{ s}^{-1}$. A laser-extensometer (Fiedler) monitored the strain directly at the sample. The deformation behaviour was additionally investigated in situ by high-energy X-ray diffraction ($\lambda = 0.0123984 \text{ nm}$) at the beam line BW5 of HASYLAB in Hamburg, Germany. The stress was gradually increased from 0 MPa to about 1100 MPa with a stepsize of approximately 100 MPa. Micrographs were recorded by means of a Hitachi TM1000 scanning electron microscope (SEM).

Figure 1 displays a $\text{Cu}_{10}\text{Zr}_7$ specimen after the attempt to cut it using a diamond-cutting wheel. The surface is extremely rugged and multiple cracks can be seen (inset to Fig. 1), which demonstrate the extreme brittleness of this intermetallic compound, which is why no compression test specimens could be prepared.

By contrast, the B2 phase stabilized in $\text{Cu}_{50}\text{Zr}_{50-x}\text{Ti}_x$ ($0 \leq x \leq 7.5$) and in $\text{Cu}_{47.5}\text{Zr}_{47.5}\text{Al}_5$ as well as the CuZr_2 phase all exhibit fracture strains exceeding 5% (Fig. 2). Especially, the latter two compounds deform plastically up to 15% (Table 1) and are thus far from being brittle. This is combined with work-hardening, which is extremely pronounced for the B2 compounds and which depends on the composition. When the B2 phase is produced in binary $\text{Cu}_{50}\text{Zr}_{50}$ the yield strength is highest but at the same time the fracture strength and plastic strain are lowest (Table 1). The work-hardening behaviour of the ternary alloys is much more pronounced than in the case of $\text{Cu}_{50}\text{Zr}_{50}$ and the compressive stress–strain curves show the characteristics of a so-called double yielding (see arrows in Fig. 2) [10]. With increasing Ti

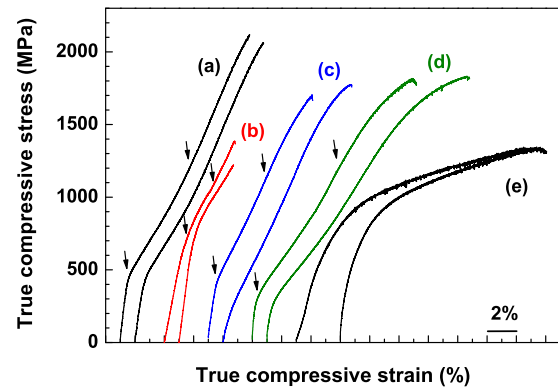


Figure 2. True stress–strain curves of the B2 phase stabilized in (a) $\text{Cu}_{47.5}\text{Zr}_{47.5}\text{Al}_5$, (b) $\text{Cu}_{50}\text{Zr}_{50}$, (c) $\text{Cu}_{50}\text{Zr}_{47.5}\text{Ti}_{2.5}$, (d) $\text{Cu}_{50}\text{Zr}_{42.5}\text{Ti}_{7.5}$ and (e) of the CuZr_2 phase. All B2 alloys exhibit a double yielding behaviour indicated by the arrows.

Table 1. Summary of the compression tests for the different B2 phases and CuZr_2 . The 0.2% offset yield strength is given.

Alloy	Yield strength (MPa)	Fracture strain (%)	Maximum stress (MPa)
$\text{Cu}_{47.5}\text{Zr}_{47.5}\text{Al}_5$	450–490	8.7–8.8	2060–2120
$\text{Cu}_{50}\text{Zr}_{50}$	710–730	3.7–4.8	1220–1390
$\text{Cu}_{50}\text{Zr}_{47.5}\text{Ti}_{2.5}$	260–460	7.1–8.7	1700–1770
$\text{Cu}_{50}\text{Zr}_{42.5}\text{Ti}_{7.5}$	200–290	11.2–14.3	1810–1830
CuZr_2	460–560	14.0–16.0	1330–1340

content the yield strength drops and the double yielding becomes more distinct. The latter effect is also found in Ti alloys [10] as well as NiTi-based alloys [11] and is linked to a change in the deformation behaviour from being borne by a martensitic transformation to a process mediated by dislocation movement [10]. An increasing Ti content causes the slope of the dislocation-borne hardening for the B2 phase to decrease and at the same time to increase the plastic strain associated with this process (Fig. 2).

In order to reveal the cause of the work-hardening and plasticity, in situ deformation experiments were performed in synchrotron radiation for all alloys, and the result is exemplarily depicted for $\text{Cu}_{47.5}\text{Zr}_{47.5}\text{Al}_5$ in Figure 3. The strongest reflections all stem from B2 CuZr (Pm-3m) and the lattice constant was determined to be

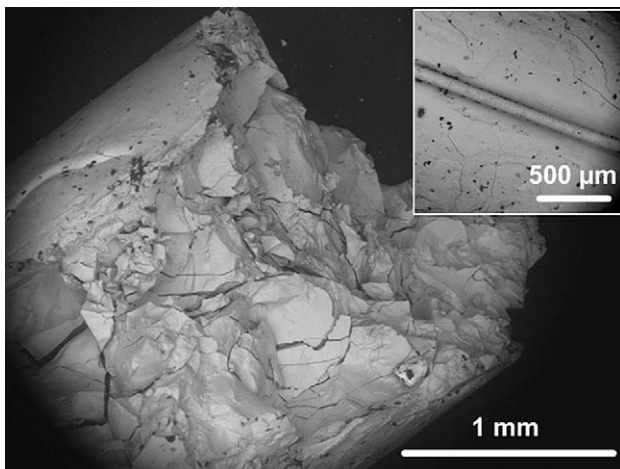


Figure 1. $\text{Cu}_{10}\text{Zr}_7$ rod with a diameter of 2 mm after the attempt to cut it. The surface is extremely rugged and cracks can be seen on the lateral surface of the rod in the as-cast state (inset).

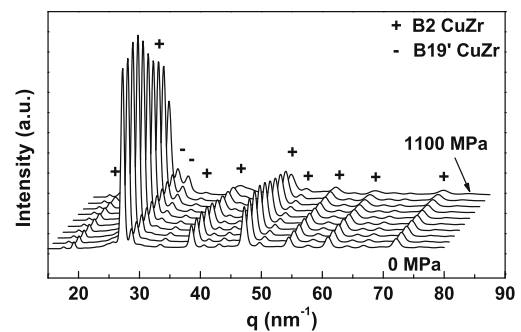


Figure 3. In situ X-ray diffraction during compressive loading of the B2 phase in $\text{Cu}_{47.5}\text{Zr}_{47.5}\text{Al}_5$. With increasing load that the B2 reflections become weaker and additional reflections of martensite appear.

$a_0 = 0.3264$ nm, which is in good agreement with literature data [12]. The intensity of the B2 CuZr reflections decreases and the peaks significantly broaden during deformation. Furthermore, additional reflections corresponding to martensitic CuZr (B19' and B33) [13] appear and become more pronounced. This proves that there is a deformation-induced martensitic transformation in the B2 phase, and the strong work-hardening as well as the plasticity must be attributed to this transformation (transformation-induced plasticity, TRIP).

A large number of AB intermetallic compounds with a B2 structure constitute the exception from the rule that intermetallics are intrinsically brittle [14,15]. Gschneidner et al. could show that the ductility of some B2 intermetallics is related to their low Poisson's ratio [14] and to the density of states (DOS) at the Fermi level [15]. Apparently, CuZr is another example of such a ductile AB intermetallic compound with a B2 structure, in which the martensitic transformation additionally enhances the plastic deformability and causes pronounced work-hardening. The compression test results (Fig. 2) imply that proper tuning of the alloy composition can be very effective for tailoring the deformation behaviour of the B2 phase.

From Table 1 it clearly follows that the yield strength of CuZr₂ is slightly higher than for the ternary B2 phases tested but the fracture strength is nevertheless lower. Consequently, the work-hardening of CuZr₂ is much less pronounced and it appears that a different deformation mechanism is active. Also the structure of the fractured CuZr₂ samples was investigated by means of high-energy X-rays (not shown here) and no phase transformation was detected. This suggests that the plasticity and work-hardening are mediated via classical dislocation generation and movement. Despite its tetragonal structure, CuZr₂ can be deformed to strains up to 16% (Table 1). It could be thus beneficial for reinforcing Zr-based BMGs in order to obtain ductile BMG matrix composites and recent results seem to corroborate this hypothesis [16].

In this final paragraph a possible relation between the plasticity of Cu–Zr BMGs and the corresponding intermetallic phases shall be addressed. All three intermetallics explored in this work, B2 CuZr, Cu₁₀Zr₇ and CuZr₂, melt congruently and hence these are the crystalline phases, which compete with vitrification of the respective melts. Therefore, these Cu–Zr BMGs have been suggested to be termed “intermetallic glasses” since they form at a stoichiometric intermetallic phase instead of a deep eutectic [17]. During quenching of the melt nuclei of the competing crystalline compound might be frozen into the glasses and the crystalline-like short-range order might then influence the deformation behaviour. It is widely acknowledged that the structure of BMGs inherits, at least on a short-range-scale, the characteristics of the competing crystalline phase [18]. If one stretches this hypothesis a bit more one could assume that

the mechanical properties of a given BMG might resemble those of the corresponding intermetallic phase to some degree, since the structure generally determines the deformation behaviour. This could explain why BMGs in the neighbourhood of Cu₁₀Zr₇ are intrinsically brittle [7,19], whereas Cu₅₀Zr₅₀ BMGs can be deformed irreversibly [6,7].

In conclusion, two plastically deformable intermetallic compounds were found in the Cu–Zr system. While CuZr₂ exhibits a hardening mechanism borne by dislocations, B2 CuZr undergoes a deformation-induced martensitic transformation. This results in the pronounced work-hardening and plastic strain (TRIP effect). The mechanical properties of the B2 phase are strongly influenced by the addition of third elements such as Al and Ti. The different Cu–Zr intermetallic phases seem to dictate the response of the according BMGs to mechanical loading.

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