Formation of Nanostructures in Brittle Materials with Transformations

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Abstract. Deformation and fracture of metal matrix composites under various loading schemes are studied. It is shown that in conditions far from transformation the material is deformed by dislocation glide as an ordinary crystal. In this case, yield stress is inversely proportional to the carbide spacing; in alloys with high solid phase content it is not achieved up to fracture. Fracture of the material is catastrophically brittle. Deformation tests of composites near the phase transition temperature show that there are different transformations induced by a highly non-uniform stress state of the binding phase. Under loading the transformation scheme B2-> B2+ B19->B2 + “quasi-amorphous state” is realized in the binding phase with the formation of a microcrystalline, highly misoriented structure with the characteristic size of crystallites less than 10 nm. This structure has high plasticity and strong hardening. It governs an efficient transfer of external load to solid particles, inducing dislocation glide even in typically brittle titanium carbide particles. The physical meaning of using binders with unstable structure in composites involves a decrease in the scale of the structural level of plastic deformation due to the formation of the microcrystalline structure of the binding phase during non-uniform loading.

1. Introduction
Metal matrix composites reinforced by dispersed solid particles are typified by so-called hard alloys which present a heterophase mixture of carbide particles (WC, TiC or Cr$_2$C$_2$) enclosed in a "soft" metal interlayer (such as Co, Ni, Fe or their alloys). It is well known that hard alloy production is based on a compromise between strength and hardness on the one hand and plasticity and toughness on the other hand. This is manifested by maxima appearing in the dependence of strength properties of hard alloys on composition and/or size of carbide grains. In this case, the curve shape is governed by the transition from brittle behavior of a composite under loading to plastic one. Plasticity is assumed...
here as high fracture energy of composite materials, which is determined by multiple damage accumulation in the material structure.

It is evident that an increase in strength and hardness of a hard alloy at same toughness, namely, a shift of the maximum in "strength - composition" dependences to the left, is possible only if the relaxation capacity of the binder remains the same with decreasing intercarbide layer thickness. In [1,2] were proposed to describe a plastic deformation as structural transformation in a crystal. According to these ideas, the crystal is brittle if it is not close-packed and has one stable structure. Britteness of intermetallic compounds with the B2 structure is demonstrative in this respect. Most of these compounds, e.g. NiAl [3-5], have a stable B2 structure and no other structures with approximate energy; besides, the compounds are brittle. The lattice of such a compound cannot transform under loading; crack nucleation is the only dissipative process in the deformed crystal. Among these compounds, however, there is a unique intermetallic compound TiNi that, along with the B2 structure, has the R and B19' structures similar in energy. The possibility of their easy structural transformation governs thermoeelastic martensitic transformations in TiNi and high plasticity of the intermetallic compound. While alloying of TiNi stabilizes the B2 structure and makes the compound much less plastic [6]. According to [1,2], this corresponds to the hierarchy of structural levels of deformation depending on specific loading conditions.

The analysis of the nature of low plasticity of hard-alloy composites in this context shows that plastic shear constraint in thin interlayer of the binding phase does not provide the small scale of the structural level of deformation. As a result, an alloy undergoes brittle fracture. If plastic deformation is considered as local structural transformation and structural instability in the material is provided from the very beginning, this will result in a general increase of plasticity due to a decrease in the scale of the structural level of plastic deformation.

The present paper aims at illustrating these concepts using metal matrix composites whose binding phase experiences structural phase transformation.

2. Materials and methods

Alloys are prepared by standard methods of powder metallurgy [7,8]. To study deformation and fracture, a complex investigation of specimens deformed at different stages is carried out using metallography, scanning electron microscopy of section surfaces, transmission electron microscopy of coal replicas, section and fracture surfaces and thin foils as well as using X-ray structural analysis. The system is deformed both close to the critical temperature of martensitic transformation (T~Ms) and at much higher one (T>>Ms). Besides, transformation temperatures change due to additional alloying of a composite with titanium, so that the martensitic transformation temperature $M_s$ increases from 77 K (an alloy without alloying addition) to room one which is the deformation temperature. During the experiment specimens are consistently loaded up to different degrees of plastic deformation.

3. Results and discussion

Investigations of deformation and fracture of TiC-TiNi alloys near the structural transition temperature show that deformation of titanium nickelide during shear instability loss by its lattice is accompanied by considerable changes in the structural state. Even in initial undeformed specimens of TiC-TiNi composites titanium nickelide has a rather heterogeneous structure. A characteristic contrast in the form of ripples in bright-field electron microscopic images testifies that titanium nickelide is in the pretransition state with the structure of short-range order of displacements [9]. In undeformed alloys the martensite phase is present as lamellae primarily in large binder interlayers. Transformations are observed in TiNi during loading. Their different character is governed by highly non-uniform stress state of the binder in such a composite material. The structure changes by the following mechanisms. During loading the titanium nickelide microstructure changes from a dispersed domain to lamellar structures even in the region of elastic behavior of the composite. Such a structure is typical of intermediate shear structures. In electron-diffraction patterns diffusion spots and then
extra reflections appear both in commensurable and incommensurable locations with different commensurability parameters and in different directions of the reciprocal lattice. This suggests that several variants of premartensite domains with different structure in each domain are formed. The observed character of TiNi transformation is induced by a very complex stress state around solid particles during composite loading. At high stress gradients in the binder stress conditions at a given loading moment in a given binder microvolume determines directions of atomic displacements in micro-regions, which determine local losses of stability by the B2 structure.

Figure 1. (a) - The electron diffraction of deformed binder in composite in initial stage of deformation. (b) - The quasi-amorphous state of a binder before fracture.

At strains above the elastic limit of the composite a dispersed structure is formed in most stressed regions of the binder. It consists of misoriented fragments of the B2-phase and martensite domains. In the bright field these regions have a non-uniform contrast including black, gray and white differently sized zones. Electron-diffraction patterns of these regions present typical rings (fig. 1a). An intense broad ring distinguished clearly among others has a width corresponding to an interplanar spacing range of 0.240-0.201 nm. It includes the strongest reflections of the monoclinic phase B19 (002), (111), (020) and the strongest reflection of the cubic structure (110)-B2. At high deformation of the composite one can see zones of almost uniform intensity in some binder regions (mainly, near carbide boundaries and in thin intercarbide layers) (Fig. 1b). In electron-diffraction patterns these regions appear as continuous diffusion rings (110)-B2 that sometimes contain arcs in main azimuthal directions. Such a character of reflections corresponds to a quasi-amorphous matter. The martensite structure in the form of plates, which exists in the initial state, disappears completely.

The X-ray analysis shows that during composite loading both the integral and peak intensity of B2 phase lines decreases simultaneously (Fig. 2), which bears witness to its transformation to another structure without appearance of martensite lines. This can result from high dispersity of the formed martensite phase, which is observed by electron microscopy.

The results obtained testify that after high deformation of TiC-TiNi a heterogeneous structure consisting of micro-domains of the martensite phase and regions of the dispersed and quasi-amorphous B2 phase is formed in titanium nickelide. A similar situation is observed after severe rolling deformation of TiNi alloys [10] and after deformation of titanium nickelide in Bridgman's chamber, which leads to the total amorphization of the B2 phase [11].

It is important to note that the character of transformations, when a heterogeneous highly refined structure is formed in titanium nickelide under deformation of the composite material, hardly depends on the interparticle layer thickness and is realized under considerable compressive stresses within the composite.

The result obtained strongly supports the character of deformation predicted in [1, 2] in a shear-unstable crystal near structural phase transitions. Even under weak general deformation of the composite a misoriented microcrystalline structure formed in such a crystal at structural heterogeneity. A low structural level of binder deformation cannot but influence the behavior of the composite material under loading.
An important conclusion follows from the mentioned experimental data, namely, a decrease in the structural deformation level of the binder (e.g. formation of a misoriented highly refined structure) provides load transfer to solid particles. This governs consistent deformation of phases and consequently macrodeformation of the composite as a structural whole.

A composite material with the binding phase in the transformation zone is characterized by a considerable increase in toughness. For comparison on Fig.3 presents stress-strain curves for a TiC-TiNi composition with the binder in the stable state and in the transformation zone. In the latter case, a considerable portion of plasticity (up to 6 %) appears in the strain curve. Fracture energy rises in a similar manner. In this case, strength does not decrease and even increases slightly.

The deformation pattern also differs considerably. Thus, with strain growth in the TiC-TiNi system at $T\sim M_s$ carbide particles are effectively loaded as a misoriented highly refined structure is formed in the binder. Under stresses above the elastic limit of the composite dislocation glide is activated in titanium carbide (Fig. 4). Multiple slip within carbide particles bears witness to a complex triaxial stress state. Loading of solid particles is accompanied with their multiple cracking.

Plasticity and strength of titanium nickelide are simultaneously combined in TiC-TiNi alloys due to a specific deformation character of the binder material in the transformation zone, where a heterogeneous structure is formed with binder fragment rotations increasing with strain growth (Fig. 5a,b). Deformation of the binder can be represented as viscous flow with gradual structure transformation. As simultaneous combination of plastic deformation and phase transformation provides high plastic properties of such a system.

The mutual rotation of carbide particles without continuity violation should be assigned to one of deformation mechanisms of such a composite material under high loading. In this case, rotation increases as carbide particles become smaller (Fig. 5c). A thin binder layer is extruded to the surface, which bears witness to strong deformation localization in an intercarbide layer. Carbide particles rotate as a whole. The diffraction pattern of the binding phase corresponds to the material structure after...
rolling (in set in Fig. 5a). Evidently that such mutual displacement of particles is possible only at arbitrary deformation of the binder. Transition to macromotion of structure elements of the composite as a whole provides an increase in material plasticity. Thus, low strains in the binding phase from the very beginning of composite loading, which is manifested in the formation of a highly refined misoriented structure, determine the character of subsequent deformation and fracture of the composite material. High relaxation capacity of the binder governed by structural transformations in it as well as a special type of hardening resulting from this lead to plastic loading and cracking of solid particles. The involvement of the solid phase in deformation provides consistent deformation of binder particles. Consistent deformations of structural constituents, mutual rotation and displacement of solid particles induced by arbitrary deformation of the binder govern transition to macromotion of structure elements and deformation of the composite as a whole.

Toughness stems from effective energy dissipation during composite loading due to both high relaxation capacity of the binder and multiple cracking of carbide particles. The latter is provided by a special type of binder hardening without plasticity loss. Thus, the structural level of binder deformation is of principal importance for the deformation character of a heterophase material. If from the very beginning of loading the binder is deformed by vortex flow rather than translational shear, which is possible in shear-unstable crystals close to structural phase transition, then a simultaneously plastic and high-strength composite material can be obtained. As mechanical characteristics of composite materials are additive, binder transformation accompanied by a decrease in its elastic modulus inevitably leads to a decrease in composite rigidity. Rigidity is usually increased by adding a solid reinforcement. However, the ultimate strength decreases in this case.

The latter is not observed in alloys with structural phase transformations and the high damping capacity of the binder leads to a shift of maximum strength properties to a higher content of the solid phase. Thus, with retention of strength and hardness, toughness of a hard alloy can be substantially increased due to a controlled decrease in stiffness using a binder with unstable structure. This is illustrated in Fig. 6 that represents data on strength properties of TiC-TiNi alloys with the martensitic transformation temperatures Ms=77K and 300K. As expected, the maximum in the “bending strength-binder content” dependence is seen to shift to a lower content of the binding phase. Transformation in the binder influences mainly composite plasticity.

4. Conclusions
The investigations conducted have shown that in conditions far from transformation the hinder material is deformed by dislocation glide as an ordinary BCC crystal. In this case, the yield stress of the binder is inversely proportional to the carbide spacing; in alloys with high solid phase content it is not achieved up to fracture. Cracks are generated along weakest regions, namely, carbide - carbide and carbide -binder interfaces. Material fracture is catastrophically brittle. The study of alloy deformation close to the structural transition temperature has shown that there are transformations in the binding phase. They are different in character, which is governed by a highly non-uniform stress state of the binder. During loading even in the region of elastic behavior of the composite the titanium nickelide microstructure changes from a dispersed domain to banded structure. The latter is typical of intermediate shear structures. In electron-diffraction patterns diffusion spots and then extra reflections appear both in commensurable and incommensurable locations with different commensurability parameters and in different directions of the reciprocal lattice. This character of
TiNi transformation is induced by a very complex stress state formed around solid particles during composite loading under high stress gradients arising in the binder. At strains above the elastic limit of the composite the dispersed structure consisting of misoriented fragments of the B2 phase and martensite domains is formed in binder region under most stressed conditions. Electron-diffraction patterns of these regions have typical rings. At high deformation of the composite one can see zones with almost uniform intensity in some binder regions (primarily near carbide boundaries and in thin intercarbide layers). These regions give continuous diffusion rings (110)-B2 in electron-diffraction patterns that sometimes contain arcs in main azimuthal directions. Such a diffraction character corresponds to a quasi-amorphous matter. Thus, during deformation the transformation scheme B2=>B2+R19=>B2+"quasi-amorphous state" is realized in the binding phase with the formation of a microcrystalline, highly misoriented structure with characteristic size of crystallites less than 10 nm. This structure has high plasticity and strong hardening. It governs an efficient transfer of external load to solid particles, inducing dislocation glide even in typically brittle titanium carbide particles. The physical meaning of using binders with unstable structure in composites involves a decrease in the scale of the structural level of plastic deformation due to the formation of the microcrystalline structure of the binding phase during non-uniform loading.

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