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Amorphous and crystalline phases in rapidly solidified Al–Ta and Al–Ta–V alloys

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Abstract

Al–Ta and Al–Ta–V alloys with composition corresponding to complex crystalline phases have been prepared by rapid solidification in order to examine the ability of these systems to form quasiperiodic or amorphous phases. According to transmission electron microscopy investigation, the rapidly solidified alloys show crystalline phases together with an amorphous phase having a high Ta content. TEM observations carried out on ground samples indicate that the crystalline phases transform into a nanocrystalline structure under mechanical grinding.

Keywords: Amorphous materials; Nanostructured material; Rapid solidification; TEM

1. Introduction

In the search for amorphous materials, the existence of deep eutectic in the phase diagram has been a successful criterion to determine composition with good glass forming ability. However, amorphous states and quasiperiodic structures have also frequently been found in rapidly solidified alloys with composition close to complex crystalline phases. Actually metallic systems displaying complex crystalline structures often show quite narrow composition range in which several complex phases can be found. Since complex phases are usually build of similar clusters, the presence of numerous complex phases illustrates the tendency of clusters to pack in different ways. In that respect the Al–Mn system is a typical example of high degree of structural complexity within quite limited composition range. As the clusters involved are usually based on icosahedral packing, such a sensitivity of structure to composition may be reminiscent of the geometrical frustration related to the forbidden icosahedral symmetry. The structural approach is then attractive for anticipating compositions of long range ordered phases or amorphous ones. The first icosahedral phase discovered in Al14 at%Mn alloys as well as the phases with decagonal or octagonal symmetry illustrate this point of view since they all correspond to composition close to complex crystalline phases [1]. Similarly, the Al61 at%Mg incommensurately modulated phase composition was determined from consideration on the crystalline structures found in this range [2]: in particular, Al_3Mg_2, a complex cubic crystalline phase ($Fd3m$, $a = 2.8$ nm) with 1132 atoms per cell [3], $Mg_{17}Al_{12}$ ($I43m$, $a = 1$ nm) isostructural of the α-Mn phase, a complex tetrahedrally packed phases known for its anomalous topology [4].

Following this line, rapidly solidified Al–Ta and Al–Ta–V alloys have been elaborated in the search of new structures or amorphous phases. This system was chosen because of its similarities with the Al–Mg system. In particular, one can find a face centred giant cell structure $Al_{69}Ta_{39}$ ($F43m$, $a = 1.9$ nm, Pearson symbol: cF432 [5]) and several other complex phases [6] including $Al_{12}Ta_{17}$ ($I43m$, $a = 1$ nm), an α-Mn isostructure. The Al–Ta–V is also an interesting point for comparison with the Al–Ta system since it exhibits also very complex phase [7]. However, for the Al–Ta–V alloy, according to the phase diagram [8], the V content is taken lower than the τ phase one to remain close to the Al–Ta binary system behaviour. The studied alloys have the following compositions Al64 at%Ta36 at% ($Al_{69}Ta_{39}$) and Al57 at%Ta36 at%V7 at% ($Al_{62}Ta_{39}V_7$).

The rapid solidification drives materials far away their thermodynamical equilibrium and hence allows to form non-equilibrium structures. Other processes, such as mechanical alloying are also known to induce structural transformation.

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From this point of view, the Al–Ta system is also of interest since repeated cold rolling on Al–Ta multilayers has revealed amorphization [9]. Therefore, in the course of the present TEM investigation, the microstructure of alloys prepared by ion beam thinning was compared to samples prepared by grinding.

2. Material and methods

Alloys have been prepared from pure elements by induction melting in a water-cooled inductive copper crucible in a He flow. Rapidly solidified ribbons were obtained using an advanced variant of melt spinning technique (Planar Flow Casting). Ingots 5–10 g are melted in a quartz nozzle under helium and ejected on a rotating copper based wheel (20 m/s). The ribbons were further examined by X-ray diffraction and transmission electron microscopy (TEM) coupled with energy dispersive X-ray (EDX) analysis. From the as prepared ribbons (approximately 50 μm thick), two kinds of samples for TEM were prepared either by ion beam milling (4 keV, 10°) or by manual grinding.

3. Results

3.1. Rapidly solidified Al–Ta and Al–Ta–V alloys

Fig. 1a gives the typical microstructure by the Al–Ta ribbons prepared for TEM observations by ion beam milling. Two kinds of grains approximately 100–300 nm large (Fig. 1) are observed. The dark grains consist of a crystalline phase identified as the complex cubic $Al_{69}Ta_{39}$ structure, the cF432 phase after its Pearson symbol [2]. The dark grains are characterized by a high density of stacking faults, a usual feature of complex metallic alloys. According to EDX analysis, the composition varies from Al75 at%Ta25 at% to Al65 at%Ta35 at%. This composition range is not due to analysis artefact since the X-ray absorption correction is only about 1 at%. Some of the bright grains are consistent with a DO_{22} structure with a composition close to Al_3Ta. The smaller bright grains in Fig. 1a are amorphous according to their diffraction patterns (Fig. 1). Fig. 1b shows a diffraction pattern of an amorphous area together with some contribution of a neighbouring crystalline grain. The ring characteristic of the amorphous phase is very pronounced. This amorphous phase is not due to some preparation artefact since, as shown by Fig. 1c, the diffraction pattern (here a (1 0 0) zone axis) of the cF432 structure does not show any diffuse rings. As reported in Fig. 1d, the amorphous phase composition is close to Al40 at%Ta60 at%. EDX analysis repeated on several amorphous grains show that the amorphous grain composition is in the Al48 at%Ta62 at%–Al42 at%Ta58 at% range. Such composition reminds of the $Al_{12}Ta_{17}$ phase (Al42 at%Ta58 at%), which is isostructural of the complex α-Mn structure.

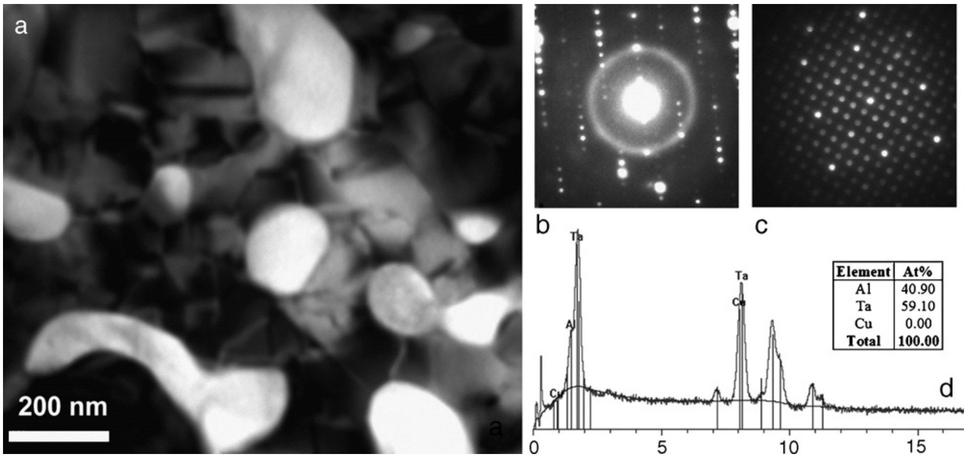


Fig. 1. Microstructure of the Al64 at%Ta36 at% rapidly solidified alloys. (a) Bright field image showing the coexistence of bright and dark grains, dark grains being heavily faulted have a strong crystalline contrast while the bright ones are homogeneous. (b) Diffraction pattern taken in a bright grain showing a pronounced diffuse ring characteristic of amorphous phase. (c) Diffraction pattern of a dark grain, this four-fold pattern is consistent with the cF432 structure. (d) EDX spectra and analysis results for an amorphous grains (the Cu signal on the spectra is due to the sample holder and is further deconvoluted in the analysis).

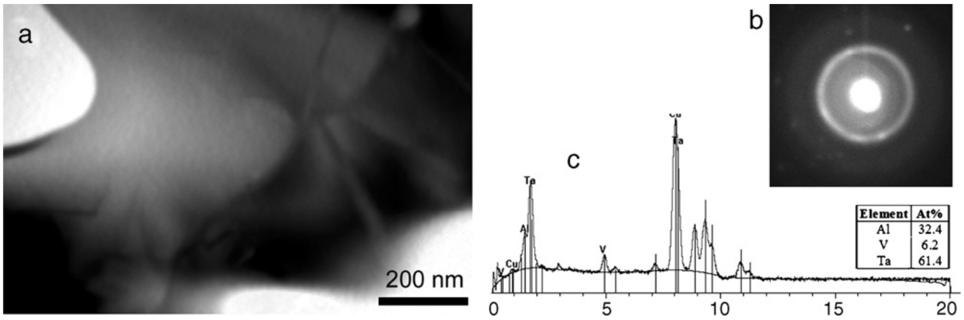


Fig. 2. Microstructure of the Al57 at%Ta36 at%V7 at% rapidly solidified alloys. (a) BF image of an amorphous area coexisting with a crystalline grain. (b and c) Diffraction pattern and composition given by EDX for the amorphous grain.

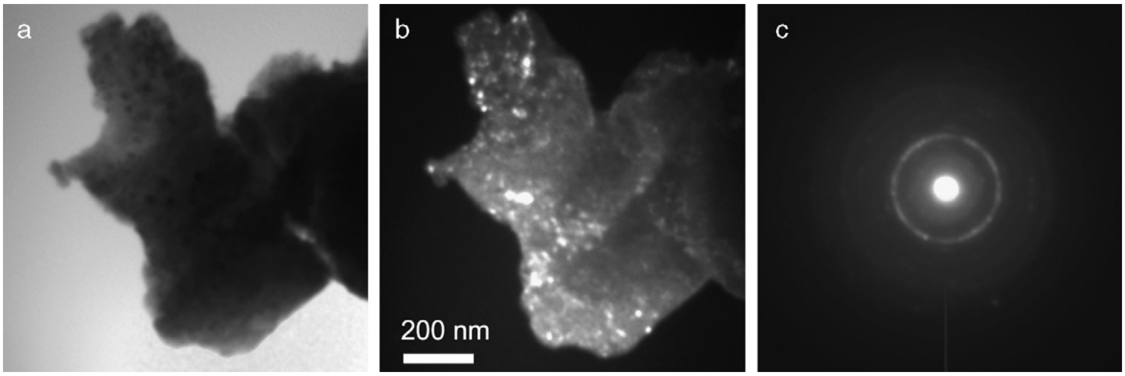
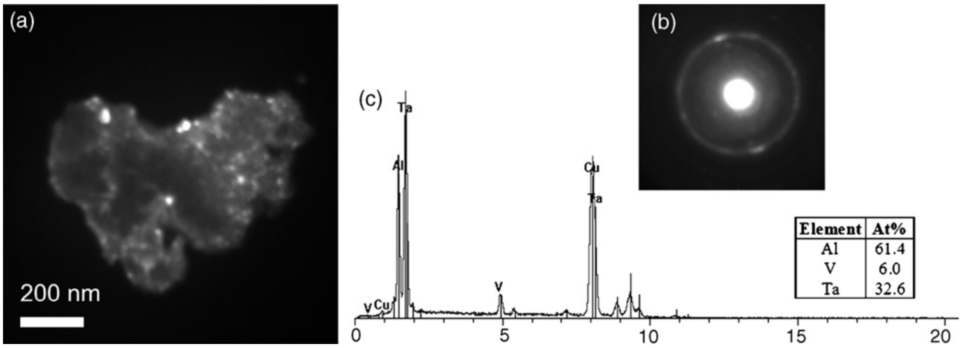


Fig. 3. Microstructure of the Al64 at%Ta36 at% rapidly solidified alloys after grinding. (a and b) BF and DF images showing ∼20 nm size nanocrystals within the grains. (c) Diffraction pattern taken on the grain in (a) showing no spot pattern but a ring one indicating that the whole grain is nanocrystalline.



Element	At%
Al	61.4
V	6.0
Ta	32.6

Fig. 4. Microstructure of the Al57 at%Ta36 at%V7 at% rapidly solidified alloys after grinding. (a) DF image showing ∼20 nm size nanocrystals within the grain. (b and c) Diffraction pattern and composition of the grain in (a).

In the Al57 at%Ta36 at%V7 at% rapidly solidified alloy, on the samples prepared by ion milling, an amorphous phase is also observed as well as one crystalline phase. In Fig. 2a is shown the coexistence of an amorphous zone and a crystalline one. The crystalline grain structure corresponds to the cF432 complex phase. The composition of the amorphous grains (Fig. 2b) is Al32 at%Ta61 at%V7 at% (Fig. 2c).

In the rapidly solidified alloys, the major point is that in both cases amorphous grains are present. They coexist with the high temperature structures expected from the phase diagram. In both cases, the composition of the amorphous grains is rich in Ta and close to the one of the complex $Al_{12}Ta_{17}$ phase.

3.2. Microstructures obtained after grinding

Ribbons of the Al64 at%Ta36 at% rapidly solidified alloys have been ground into powder in a mortar and then examined by TEM. Fig. 3 shows the microstructure observed in the grains having a composition in the range corresponding to the dark grains in Fig. 1, i.e. the crystalline grain having the cF432 structure. According to the bright field and dark field image in Fig. 3a and b, the grains appears as nanocrystalline, the crystallite size being approximately 20 nm. As illustrated by the diffraction ring in the diffraction patterns (Fig. 3c), the whole particle is nanocrystalline.

Similarly, nanoscrystallisation has been observed in the Al57 at%Ta36 at%V7 at% after grinding of rapidly solidified alloys. Fig. 4 shows a grain (Fig. 4a) together with its diffraction pattern (Fig. 4b) and the EDX analysis indicating that the grain composition was the one of a crystalline cF432 structure before grinding.

4. Concluding remarks

This study has pointed out that, in rapidly solidified Al–Ta and Al–Ta–V alloys, an amorphous Ta rich phase is formed. The present results show that the amorphous phase corresponds to a 60 at% Ta content. This composition is reminiscent of $Al_{12}Ta_{17}$, a phase with a classically ill-defined structure, the α-Mn structure-type [3]. Actually, the Ta content seems to have a key role in this alloy regarding the glass forming ability. The succession of peritectic reactions, in the phase diagram, leading to the formation of intermetallic phases between Al and Ta with high negative enthalpies of mixing, is not favoring here complete amorphisation.

Regarding the effect of strain, the microstructure after grinding indicates a strong ability of the complex crystalline cF432 to form nanostructures. This point could be of particular interest for interpretation of the nanocrystallisation of cold rolled $Al_{75}Ta_{25}$ multilayers [9].

References

[1] C. Janot, Quasicrystals, A Primer. Monographs on the Physics and Chemistry of Materials, vol. 50, second ed., Clarendon Press, Oxford, 1994.

[2] P. Donnadieu, H.L. Su, A. Proult, M. Harmelin, G. Effenberg, F. Aldinger, J. Phys. I France 6 (1996) 1153–1264.
[3] S. Samson, Acta Crystallogr. 19 (1965) 401–413.
[4] F.C. Frank, J.S. Kasper, Acta Crystallogr. 11 (1958) 184–190.
[5] S. Mahne, B. Harbrecht, J. Alloys Compd. 203 (1994) 271–279.
[6] P. Villars, L.D. Calvert (Eds.), Pearson's Handbook of Crystallographic Data for Intermetallic Phases, vol. 2, second ed., ASM International, Ohio, 1991.
[7] B. Harbrecht, N. Rheindorf, V. Wagner, J. Alloys Compd. 234 (1996) 6–11.
[8] G. Petzow, G. Effenberg (Eds.), Ternary Alloys: A Comprehensive Compendium of Evaluated Constitutional Data and Phase Diagrams, VCH, Weinheim, 1993.
[9] H. Sieber, G. Wilde, J.H. Perepezko, J. Non-Cryst. Sol. 250–252 (1999) 611–615.