Effects of Si and Nb additions on CuAlNiTi rapidly solidified alloys microstructures

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Abstract. Intensive investigations have been carried out on CuAlNiTi shape memory alloys (SMAs) with 1wt.%Ti and Ni content from 5 to 6 wt%. In this present work, we used a rapid solidification technique to prepare alloys of two compositions: (wt%) Cu₇₉Al₁₃Ni₅Ti₂Si₁, Cu₇₉Al₁₃Ni₅Ti₁Nb₂. The ribbons obtained were characterised by means of XRD, DSC measurements and TEM observations. XRD patterns indicated that the first alloy has a two-phase structure with beta and martensite 18R phases, whereas the second one is only beta. DSC measurements gave characteristic transformations temperatures. The Si-containing alloy showed low temperature transformations with M_s about -88°C and A_f at -41°C in as-quenched state. The Nb-containing alloy exhibited high temperature transformations with A_f about 170°C in the as-quenched state, which is quite higher for this alloy family. The transformation temperatures are stabilised after only one cycle at $\Delta T_M = (M_s - M_f)$ constant for both alloys. This stabilisation is likely to be generated, in the case of Cu₇₉Al₁₃Ni₅Ti₁Nb₂, by nanocrystalline precipitates revealed on TEM micrographs. Narrow and faulted martensite plates have been observed in agreement with previous results on rapidly solidified CuAlNiTi SMAs.

1. INTRODUCTION

CuAl single crystal SMA alloys have good shape memory effect (SME) whereas the polycrystalline alloys exhibit poor mechanical properties such embrittlement. Since they are attractive for SME applications, intensive studies have been conducted focused on some additive chemical elements in order to improve the ductility by avoiding intergranular fractures. Nickel addition up to 4wt.% is found to stabilise the β phase [1] and to improve mechanical properties [2] but decrease the transition temperatures [3]. Over 5wt.% of Ni, it causes embrittlement due to the spinodal decomposition of the β phase [4]. Titanium addition [5, 6] produces grain refinement and manganese [7] as well as boron [8] increase significantly the transition temperatures over 100°C.

Few CuAlNi based alloys were prepared by rapid solidification methods [9,10] compared to those obtained by conventional casting. The ability of those methods to suppress some material shaping steps has been giving more interest to the rapid quenching techniques. The yielded ribbons have fine grains and good mechanical properties [11]. In contrary, the transition temperatures [9,12] are lowered (around and under room temperature) with respect to the bulk alloys.

Here we report results on CuAlNiTi based alloys with addition of Nb and Si produced in ribbon shape that present an opposite behaviour in relation to the added elements.

2. EXPERIMENTAL

The alloys have been prepared from good purity components: Cu (99,999), Ni (99,9), Al (99,999), Ti (99,8), Nb (99,9). Pre-alloying of the components, previously carefully cleaned and weighed in the right proportions was carried out by induction melting in a water-cooled crucible. A second induction melting in electromagnetic levitation has been performed, with an overheating above the liquidus temperature in order to ensure a good chemical homogeneity. The alloys have then been rapidly solidified by the planar flow casting technique at 19 m/s (rotation wheel speed), leading to a quenching rate of about 10⁶ °C/s. The materials obtained for both alloys, are ribbons of 60µm thick, 10mm wide. They are rather ductile, for instance a sheet of 15mm length could be bent bringing the two edges in contact. Samples cut from the ribbons have been investigated by means of DSC and XRD techniques using CuK α radiation. Thin

foils from the above samples have been etched either electrolytically and by ion milling for MET observations on a Jeol Cx II operating at 120KV.

3.RESULTS

3.1 CANTNb alloy

DSC curve on figure 5 indicates that CANTNb alloy undergoes a transformation at about 110°C during first heating. After 2 thermal DSC cycles in the temperature range going from room temperature to 300°C, transformation temperatures are clearly raised giving: Ms(99) and Mf(48). The martensite transformation temperatures are quasi stable whereas some slight variations are found in As and Af positions (see table 1). The DSC results show that the alloy has some amount of stable martensite at room temperature.

Table 1: Transition temperatures for CANTiNb and CANTSi alloys; each run temperatures are listed.

Alloys	Ms °C	Mf °C	As °C	Af °C
CANTNb	(99)(99)	(48)(48)	(110)(66)(73)	(170)(180)(183)
CANTSi	(-88)(-88)(-88)	(-122)(-137)(-137)	(-76)(-80)(-80)	(-41)(-38)(-38)

XRD patterns of as-quenched (Figure 7) sample confirm the presence of martensite but also indicate that the alloy is two-phased with peaks corresponding to the β phase. The characterisation of the martensite peaks leads to a martensite 18R. The microstructures of the alloys are reported on figure 1. Narrow and faulted 18R martensite (figure 1.a and b) with variable plate with 30-60nm are observed along with no-martensite regions. Some areas within the thin foil present two types of martensite, 2H with 18R. Martensite variants accommodation (figure 1.b) are observed and also some single crystals of martensite figure 1.a. Between some plates of martensite, precipitates of quasi-similar size are also observed. The no-martensite areas contain spherical-like precipitates of about 30-100nm size on figure 1.c. similar to γ_2 precipitates [9, 13]. They are themselves containing lower sized (Xss) precipitates. DF image on figure 1.d with selected spot (see arrow) on SAD pattern shows the size evolution (about 30nm and less) and the morphology of these precipitates.

Figure 1: TEM micrographs of as-quenched CANTiNb alloy at room temperature:
a) narrow and faulted accommodated martensites,
b) DF image -selection, see arrow- showing martensite plates,
c) γ_2 precipitates in no-martensite area,
d) DF image -selection, see arrow- of small and very small (Xss) precipitates

After 2 more thermal DSC cycles from room temperature to 300°C, the transition temperatures are stabilised (table 1). The subsequent microstructures observed in thin foil are presented on figure 2. The feature of martensite variants is similar to the as-quenched sample (Fig. 2a). The martensite plates are variable in the same range than in the as-quenched sample. Furthermore, the grains in the microstructure seem well-defined. They still contain small (Xs) [14] and very small (Xss) precipitates (Fig. 2.b and c) with a size about 300nm and less (few nanometers).

Figure 2: TEM micrographs of CANTiNb alloy after 3 thermal DSC cycles:
a) martensite variants
b) DF image (selection, see arrow on SAD pattern) spherical Xs and Xss precipitates,
c) nano (1) (Xss) and small (2) (Xs) precipitates embedded in single grains.

3.2 CANTSi alloy

In as-quenched state, the CANTSi alloy is austenitic at room temperature which was confirmed both by DSC (Figure 6) measurements and XRD spectra (figure 8). The martensitic transformation occurs at low temperature under room temperature at about -88°C (Ms) and -122°C (Mf). This alloy is then a low transition temperature alloy close to the wide range of CANTi system [13].

After 2 more DSC thermal cycles, the transformation temperatures for both martensite and austenite are stable at about -88°C(Ms), -137°C(Mf), -80°C(As), -38°C(Af). The stabilisation of the alloy structure has come out only after one cycle.

TEM observations performed on thin foil of this alloy are reported on Figure 3. Microstructure of an ordered phase is observed on Figure 3.a. Eutectic phase-like grains appear on figure 3.b. In the same area, microstructure similar to PAPBs [5] is also observed in single grain shown on figure 3.c. Some of the eutectic-like grains contain quasi spherical precipitates of about 60nm size. SAD patterns (inset, figure 3.a) related to both α ordered phase (α_2) [15] and β phase. The α_2 phase is not visible on XRD spectra (Figure 8) where the main lines fit with the β phase.

Figure 3: TEM micrographs of CANTSi as-quenched alloy:

- a) α_2 phase with PAPBs,*
- b) eutectic-like structure with single phase grain containing small (Xs) precipitates,*
- c) Single crystal showing fringes similar to APBs.*

In the sample submitted to 2 more DSC thermal cycles, the α_2 phase is still observed (fig.4.a). Another area in the thin foil gives nano-precipitated microstructure whose SAD patterns are fine precipitate -type diffraction image. A selection on intense ring yields the DF image on figure 4.b. Some polycrystalline areas are also observed in another zone of the thin foil with small cuboids precipitates. SAD patterns (Figure 4.c) confirms the presence of the α phase in the sample.

Figure 4: TEM micrographs of CANTSi alloy after 2 more DSC thermal cycles:

- a) α_2 and β phases,*
- b) DF image (selection intense ring on SAD pattern) showing the Xss precipitates,*
- c) BF image of area containing α phase with the corresponding SAD pattern (inset).*

4. DISCUSSION

The results on CANTNb alloy show that the Nb addition plays an important role in the austenite appearing temperature. The rapidly solidified CANTi alloys usually exhibit in the as-quenched state low transition temperatures around room temperature [9, 12, 13]. The amount of martensite phase in the as-quenched structure is rapidly stabilised, just after the first thermal run in the DSC device. The microstructure gives some insights of this behaviour for the CANTNb alloy. Precipitation is clearly observed on TEM micrographs with variable sizes getting down to the nanometer range. Since the martensites observed have also variable sizes, and since some of them have the same size with the embedded precipitates, the plates could not grow and therefore no or few ones increase their proportion in the structure as it could be expected. In addition the microstructure which is not homogeneous due the two-phased state and to the nature of fast quenching technique, is distributed in martensite and no-martensite zone which are also stabilised by the precipitates.

In the case of the CANTSi alloy, the Si addition seems to produce an additional grain refinement effect to that of Ti. The nano-precipitates (Xss) areas hold this suggestion as well as fine precipitates in some single crystals. The presence of α_2 phase indicates an eutectoid type transformation. This assumption is to be confirmed by more TEM investigations because the XRD spectrum does not show unambiguous peaks of the α_2 phase. The presence of both α and β phases suggests an eutectic-like transformation at higher temperature during the casting. Furthermore, the results about the 18R martensite found in CANTNb and β phase for both alloys are in agreement with the literature [14, 16]. The nature of the precipitates is not yet determined, although in the CANTNb alloy some precipitates are like γ_2 [12, 14] and the very small precipitates (Xss) could belong to the same phase [17] and In order to elucidate these points, more investigations are planned including characterisation of the precipitates and microstructures, transitions temperatures evolution after betatisation.

Figure 5: DSC curves of CANTNb alloy; first run and 2 thermal cycles in temperature range room temperature-300°C.

Figure 6: DSC curves of CANTSi alloy; first run and 2 thermal cycles in temperature range room temperature - (-200°C).

5 CONCLUSION

We have prepared by the planar flow casting technique two alloys named CANTNb and CANTSi with respective Nb and Si as additional elements.

The CANTNb alloy is two-phased at room temperature and shows higher transition temperatures; the microstructures containing variable-sized precipitates down to the nanometer. The Nb is likely to generate same sized precipitates with the martensite plate size and nano- precipitates, which stabilise the structure.

The CANTSi alloy is in turn austenitic with some amount of an ordered phase at room temperature with low transition temperatures. This structure is likely to be due to the Si which produces more additional grain refinement to that of Ti.

Figure 7: XRD spectrum of as-quenched CANTNb alloy

Figure 8: XRD spectrum of as-quenched CANTSi alloy.

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