Achievements in Mechanical and Materials Engineering

COMMENT Worldwide Congress on Materials and Manufacturing Engineering and Technology

16th - 19th May 2005 Gliwice-Wisła, Poland

COMMITTEE OF MATERIALS SCIENCE OF THE POLISH ACADEMY OF SCIENCES, KATOWICE, POLAND
INSTITUTE OF ENGINEERING MATERIALS AND BIOMATERIALS OF THE SILESIAN UNIVERSITY OF TECHNOLOGY, GLIWICE, POLAND
ASSOCIATION OF THE ALUMNI OF THE SILESIAN UNIVERSITY OF TECHNOLOGY, MATERIALS ENGINEERING CIRCLE, GLIWICE, POLAND

13th INTERNATIONAL SCIENTIFIC CONFERENCE ON ACHIEVEMENTS IN MECHANICAL AND MATERIALS ENGINEERING

Microstructure of rapid solidified Cu-Al-Ni shape memory alloy ribbons

G. Lojen[a, b*], I. Anžel[a], A.C. Kneissl[b], A. Križman[a], E. Unterweger[b], B. Kosec[c], M. Bizjak[c]

[a] University of Maribor, Faculty of Mechanical Engineering, Slovenia

[b] University of Leoben, Department of Physical Metallurgy and Materials Testing, Austria

[c] University of Ljubljana, Faculty of Natural Sciences and Engineering, Slovenia

Abstract: Cu-Al-Ni shape memory alloy (SMA) ribbons were cast by free jet melt spinning. Completely martensitic wide ribbons, containing more than 13 wt. % Al and having a single layer columnar structure, could not be obtained. All ribbons exhibit shape memory effect already in as-cast condition. Heat treatments improved the properties of the ribbons. Microstructures in as-cast and in heat treated condition are discussed.

Keywords: Technologica sciences, Materials engineering, Metallic alloys

1. INTRODUCTION

Cu-Al-Ni shape memory alloys are at present the only alternative if high transformation temperatures are required. The temperatures of martensitic transformation can be “adjusted” between –200°C and 200°C [1]. The shape memory properties are based on properties of the high temperature binary Cu–Al phase β, having a body centred cubic structure. Nickel in ternary alloys slows down the diffusion of Cu and Al; in this way Ni efficiently helps to suppress the decomposition of the parent phase β during cooling, until the M_s-temperature is reached. The optimal chemical composition is about 14 wt. % Al and 3 to 4.5 wt. % Ni [2]. Transformation temperatures decrease with increasing Al-content. At 14 wt. % Al the M_s-temperature lies already around the room temperature.

Conventional production of thin ribbons (rolling) from brittle intermetallic β–phase alloys (like Cu-Al-Ni) is time consuming, work intensive and costly. Melt spinning is one of the most suitable methods to produce thin ribbons directly from the melt. The cooling rates at melt spinning of body centred cubic alloys are in general high enough to obtain martensitic ribbons [3]. Therefore shape memory effect is exhibited already in as-cast condition.

The most important disadvantage of polycrystalline Cu-Al-Ni alloys is small reversible deformation (up to 4%) due to intergranular brake down already at low average stress levels. Among the main reasons for low failure stress are coarse structure and high elastic anisotropy ($E_{<111>} / E_{<001>} = 13$), causing high shear concentrations on the grain boundaries, figure 1a. At low wheel speeds Cu-Al-Ni ribbons consist of several crystal grain layers, at moderate wheel speeds of two, and at high wheel speeds (cooling rates) of a single columnar grain layer. In ribbons having a single layer columnar structure a fibre texture was observed [4] (Eucken-Hirsch texture) - crystallographic direction [001] of all grains is perpendicular to the ribbon surface, and directions [100] or [110] are parallel to the longitudinal ribbon-axis [4, 5], figure 1b. Both, the single layer structure as well as the fibre texture contribute to improvement of ductility. In the single layer ribbons there are less grain boundaries parallel to the ribbon surface (potential crack-initiation sites). And in case of Eucken-Hirsch texture adjacent grains have similar elastic properties in the stress-direction; consequently shear stress concentrations on grain boundaries are lower. The reversible strains of fibre textured Cu-Al-Ni ribbons reach up to 6.5 % [6] - significant improvement compared to bulk material and ribbons, consisting of several layers of equiaxed, randomly oriented grains. Maximal reversible strains can not be achieved if alloying elements like Ti, Nb, Cr, and B obstruct formation of the single layer columnar structure [4].

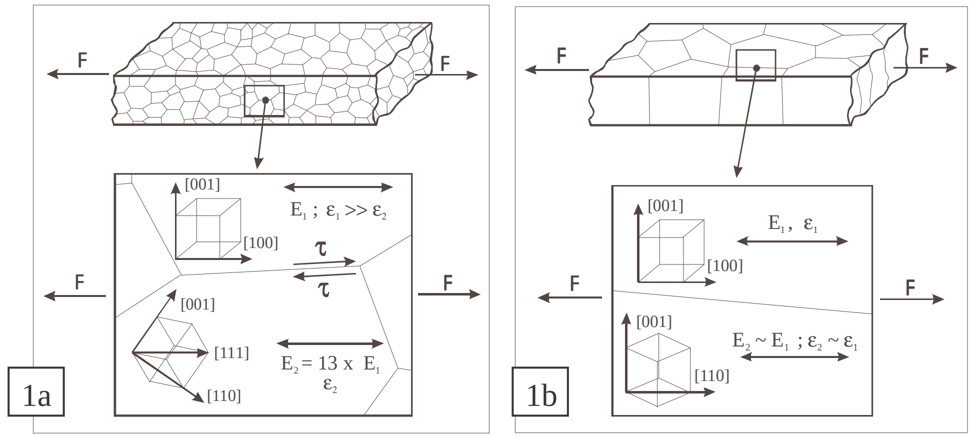

Figure 1. a) Random grain orientation - adjacent grains can have extremely different properties in load direction; b) Single layer columnar fibre textured structure-mechanical properties of adjacent grains in load direction are similar.

2. EXPERIMENTAL

Cu-Al-Ni alloys were melt-spun under a protective atmosphere (argon) in a free jet melt spinner. All alloys contained 4 wt. % Ni and: 16 wt. % Al (alloy 1), 14 wt. % Al (alloy 2), 13 wt. % Al (alloy 3) and 13 wt. % Al + 0,035 wt. % B (alloy 4). As we wanted the ribbons to be as wide as possible, relatively low wheel speeds, between 11.8 and 21.3 m/s, were selected. Some alloy 2- and alloy 3-ribbons were heat treated (annealed and water quenched) to improve the ductility. Alloy 1-ribbons were not heat treated because the required annealing temperature would be dangerously close to the alloys solidus. Samples of all ribbons were investigated in a light microscope. On alloy 1- and alloy 2-ribbon samples in as cast condition also EDX analysis in a scanning electron microscope was performed.

3. RESULTS AND DISCUSSION

The ribbons are between 25 and 240 μm thick and up to 11 mm wide. The edges are fringed, most likely because too high Reynolds-numbers of the gas boundary layer on the wheel surface.

Already the light microscopy of unpolished free surfaces allows one to make an educated guess about the phase structure of the ribbons. The alloy 1-sample (figure 1a) obviously consists of two phases. The surface morphology suggests presence of martensite. The alloy 2-sample is similar, but contains less of the non-martensitic phase on the grain boundaries. The alloy 3-ribbon seems to be fully martensitic, figure 2b.

Investigations of polished and etched samples (longitudinal and lateral cross-sections) revealed that all ribbons in as-cast condition, regardless to their chemical composition, are of non-uniform thicknesses and have a single layer columnar structure only where the thickness is under approx. 50 μm, figure 3b. Considering the grain size of 20 - 50 μm, the cooling rate must have been significantly under 10^3 K/s [7] – due to low wheel speeds and low thermal conductivity of the alloys, 30 - 43 W/mK [1].

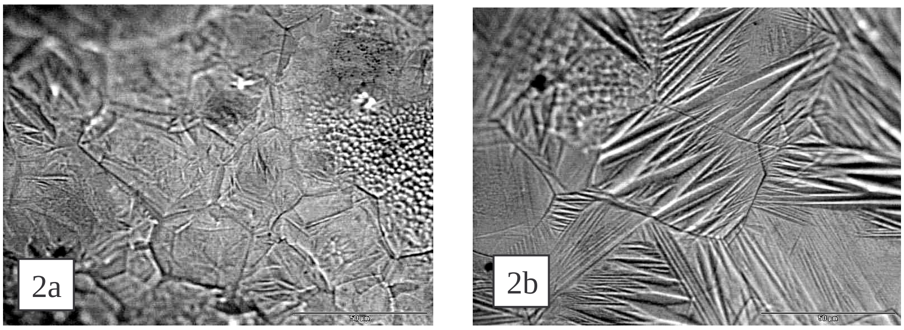

Figure 2. Free surfaces of as-cast ribbons: a) Alloy 1; b) Alloy 3.

The assumptions about the phase structure were confirmed. A polished and etched sample of the alloy 3-ribbon seems to be fully martensitic, figure 3b. Alloy 1 in fact consists of two phases, figure 3a; in the darker phase the characteristic martensite-pattern can be observed. The brighter phase must be the low-temperature phase γ_2, which precipitated because of too low cooling rate. Due to precipitation of Al-rich γ_2 the Al-content in the remaining β phase decreased and consequently M_s and M_f rose so far that martensitic transformation at least partially took place already above room temperature. Alloy 2-ribbons have a similar structure but contain less of the brighter phase on the grain boundaries.

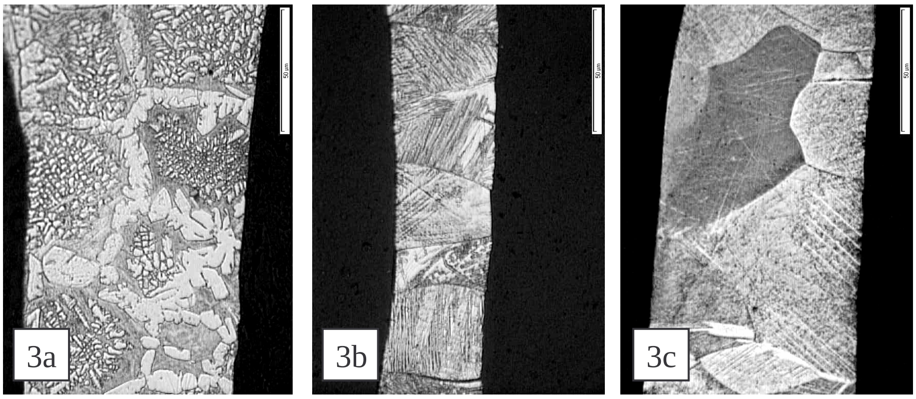

Figure 3. Phase composition of ribbons: a) Alloy 1, as-cast, partially martensitic; b) Alloy 3, as cast, martensitic; thin sections have a single layer columnar structure; c) Alloy 2, annealed for 90 s at 800°C and water-quenched, martensitic.

After heat treatment, in the light microscope also the alloy 2-ribbons seem to be fully martensitic, figure 3c. Annealing dissolved the γ_2 precipitates and the cooling rate during water quenching was high enough to suppress the precipitation of γ_2. If, beside martensite, any other phase is present, it is residual austenite; namely, with respect to the chemical composition of alloy 2, the M_f-temperature could already be below the room temperature.

The purpose of adding boron (alloy 4) was to assure a more uniform fine grained structure. By adding boron we deliberately took the risk that boron could inhibit the formation of the single layer columnar structure even in the thinnest sections. But we expected that higher ductility of thick sections due to grain refinement would overbalance the drawback of not having the favourable structure. In fact the grain size of the alloy 4-ribbons is finer; compare the figures 3 and 4b. But the thinner sections (higher cooling rate!) still have a single layer columnar structure, figure 4a (due to low B-content; higher B-contents could worsen the functional properties). Since the ductility of the ribbons increased, in spite of not obtaining a uniform fine-grained structure, alloying with boron can be regarded as successful.

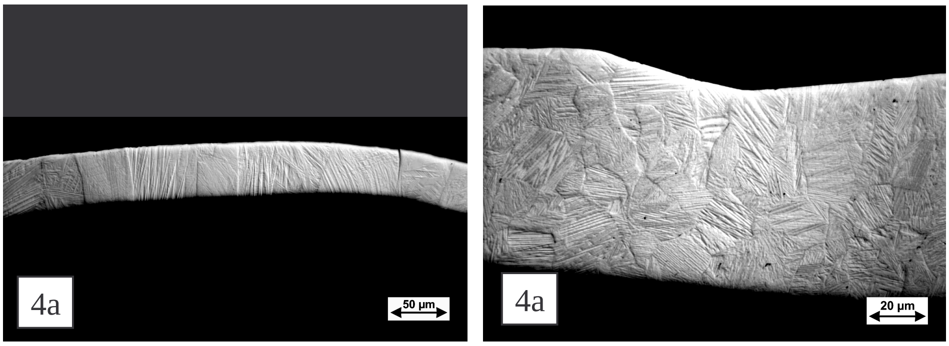

Figure 4. Microstructure of alloy 4 as-cast ribbons, interference contrast: a) Single layer columnar structure of thin sections; b) Fine-grained structure of thick sections.

The alloy 4-ribbons show the best ductility, alloy 3 and alloy 2-ribbons follow; most brittle are the alloy 1- ribbons. Heat treatment improved the ductility of alloy 2 and alloy 3-ribbons. The light microscope investigations could not reveal any significant differences between as-cast and heat treated alloy 3-ribbons. But better ductility of the heat treated ribbons indicates that in as-cast condition alloy 3 is in fact not completely martensitic, but contains small, in the light microscope undetectable precipitates of low-temperature phases which can be eliminated by heat treatment (or at least strongly diminished).

All ribbons exhibit shape memory already in as-cast condition. At heat treated alloy 3-ribbons the two-way shape memory effect could be observed already after one cycle of cold deformation and unconstrained heating.

4. CONCLUSIONS

Already in as-cast condition ribbons of appropriate chemical compositions are predominantly martensitic and exhibit shape memory effect even if spun with low wheel speeds. Because of low thermal ductility of the Cu-Al-Ni alloys, with a free jet melt spinner it is very hard to produce wide ribbons with fully martensitic single layer columnar structure. Therefore heat treatment even for melt spun material can not be avoided. Boron improves the ductility, but does not, if added in small amounts, obstruct the formation of single layer columnar structure, if the cooling rates are high enough.

REFERENCES

1. Hodgson, D.E.; Wu, M.H.; Biermann, R.J.: http://www-sma-inc.com/SMAPaper (1996).
2. Shape Memory Materials, edited by K. Otsuka, C. M. Wayman, Cambridge University Press (1998).
3. P. Donner: Die Herstellung von Bändern und Drähten aus Legierungen mit Formgedächtnis, Fortschritt-Berichte VDI, Reihe 5, Nr. 259, VDI Verlag (1991).
4. Progress in Shape Memory alloys, edited by S. Eucken, DGM Informationsgesellschaft GmbH (1992).
5. K. Bhattacharya, R. V. Kohn, Acta Materialia Vol. 44, No. 2 (1996), 529 – 542.
6. S. Eucken, J. Hirsch, Mat. Sci. Forum 487 (1990), 56-58; Reference in [12].