The results of the characterization of a CuAlNi shape-memory alloy after continuous casting technology are shown. Using this procedure a bar with a diameter of 8 mm was manufactured. After solidification of the alloy the microstructure characterization was carried out using optical microscopy (OM), scanning electron microscopy (SEM), differential scanning calorimetry (DSC) and X-ray diffraction (XRD) methods. Our results showed that the as-cast alloy consisted of the parent \( \gamma \) and martensite \( \tau' \) phases. The martensite phase as the needle-like inside grains was observed. Martensite laths have different orientations inside particular grains. It was found that the average grains size is 98.78 \( \mu \text{m} \). The grain diameter near to the external surface is higher than in the center. The average hardness of the alloy was 275 HV1.

Keywords: shape memory alloys, martensite, continuous casting, grain size

1 INTRODUCTION

Shape-memory alloys (SMAs) demonstrate the ability to return to some previously defined shape or size when they are exposed to the appropriate thermal treatment. The condition necessary to enable the memory effect is the presence of a reversible phase transformation of austenite to martensite. Such phase transformations can be obtained by mechanical (loading) or thermal methods (cooling and heating). The main types of SMAs are Ni-Ti (nitinol), Cu-based and Fe-based alloys. The main advantage of Cu-based SMAs is their low price compared to other SMAs. The properties of Cu-Al-Ni alloys are superior to those of Cu-Zn-Al alloys due to their wide range of useful transformation temperatures and small hysteresis. Cu-Al-Ni alloys can be applied at higher temperatures (close to 200 °C).

Generally, ternary Cu-based shape-memory alloys show a very large grain size. This problem can be solved by the addition of appropriate refining elements (Zr, Ti, B etc.) due to the formation of precipitates that limit the grain size and grain growth and/or by applying the technology of rapid solidification. Generally, one of reasons for using the technique of rapid solidification is to obtain a small grain size for the SMAs. The grain sizes obtained in the Cu-base are of the order of 10 \( \mu \text{m} \) in alloys produced by powder metallurgy and by rapid solidification. Melt-spinning is the most commonly used technique for the production of ribbons. In recent years the continuous casting technique is one of the technologies for production of SMAs due to the special competitive growth mechanism of the crystals and formation of a cast product with a favorable texture.

In the present paper the microstructure of Cu-Al-Ni SMAs obtained directly from the melt by continuous casting techniques are shown. The main aim of this paper was to obtain a homogenous martensite microstructure by solidification without any heat-treatment procedure.
process of casting including the initial melting and solidification was performed using a vacuum or protective atmosphere. The characterization of the alloy was carried out by optical microscopy (OM), scanning electron microscopy (SEM) equipped with energy-dispersive spectroscopy (EDS), differential scanning calorimetry (DSC) and X-ray diffraction (XRD) methods. For microstructural observations, the samples were grinded (120–800 grade paper) and polished (0.5 μm Al₂O₃). Later on, the samples are etched in a solution composed of 2.5 g FeCl₃ and 48 ml methanol in 10 ml HCl. The procedure for etching consisted of etching for 2 min, inter polishing for 2 min, and later etching for 1 min. The grain-size measurements were carried out by OM using the grain cutting line method. Hardness tests were carried out using the Vickers method (HV1). The differential scanning calorimetry (DSC) measurements were employed using a device under an argon atmosphere in the temperature range from room temperature to 300 °C. The rates of heating and cooling were 10 K/min. In order to determine the phase composition the X-ray diffraction (XRD) measurements were performed. CuKα radiation was used.

3 RESULTS AND DISCUSSION

The chemical composition analysis of the alloy was done using EDS analysis (Figure 1). The results showed that the chemical composition of the alloy was 82.73 % Cu, 13.16 % Al and 4.11 % Ni (mass fractions). The microstructures of the lateral and longitudinal cross-sections of the bar after continuous casting are characteristic of a continuously casted bar (Figure 2). Under the surface there was a layer of fine equiaxed grains followed by a region of long fringe crystals oriented towards to the centre of the cross-section where again equiaxed grains appeared (Figures 2a and b). The orientation of the crystals was changed. The fringe crystals were formed at an angle with an average value of around 60° with the longitudinal bar axis. In according to Lojen et al.¹⁹ the maximum achieved velocity of the solidification front was about 2.1 mm/s. It is possible that the crystallization front that simultaneously proceeds from the outer part of the bars to its centre causes a preferential orientation of the growing grains. The average hardness of the alloy was 275 HV1.

Figure 3 shows OM micrographs of the CuAlNi alloy after the continuous casting procedure. The grain boundaries are clearly visualized. As can be seen, the micrographs of the specimens show the typical martensite microstructure. Martensite laths have different orientations into particular grains. The grain size depends on the place from which the samples were taken. The grain diameter near to the external surface is higher than in the center.

An average grain size of 98.78 μm was observed for as-cast specimens. The number of grains per was 20.3 mm⁻². For an average grain size from 50 μm to 100 μm the fracture strain in the martensite phase is of the order of 10 %, which is sufficient for shape-memory applications. The grain size of the rapidly solidified alloys is determined by the amount of undercooling prior to the crystallization. Our results for bars after continuous casting showed that the sizes of grains vary from the surface towards the center of the bars. The increase in the grain diameter causes an increase of the $M_s$ tem-

Figure 1: EDS spectrum of CuAlNi shape-memory alloy
Slika 1: EDS-spekter spominske zlitine CuAlNi
A similar behavior was already observed for the Cu-Al-Ni-Mn and Cu-Al-Ni-Mn-Ti shape-memory alloys\textsuperscript{20} obtained using the melt-spinning technique. The temperature \( M_s \) depends on the grain size according to the relation \( \Delta M_s \propto d^{1/2} \), where \( \Delta M_s \) is the difference between the temperature \( M_s \) of the melt-spun ribbons (small grains) and the bulk alloy (large grains) and \( d \) is the mean grain diameter.

The martensitic microstructure was confirmed with the SEM micrographs (Figure 4). This microstructure is the result of the beta-phase of the Cu-Al-Ni alloys transforming into the martensite phase by cooling below the \( M_s \) temperature. The martensite is formed primarily as the needle-like shape. In some fields the V-shape...
Martensite was observed. This is a typical self-accommo-
dating, zig-zag, martensite morphology, which is
characteristic for the $\beta_1'$ martensite in the CuAlNi
alloy 21. The parallel bands in the martensite can be
considered as twin-like martensite.

Figure 5 shows DSC curves during heating and
cooling. The temperature phase transformation are:
$M_s = 215 ^\circ C$, $M_f = 169 ^\circ C$, $A_s = 229 ^\circ C$ and $A_f = 191 ^\circ C$. It can
be seen that the CuAlNi alloy is a possible candidate for
high-temperature usage. Figure 6 shows the X-ray
profile of the as-casted alloy. Our XRD analysis showed
that the alloy after continuous casting consisted of the
parent $\beta_1$ and $\beta_1'$ martensite phases.

4 CONCLUSIONS

The microstructure of a CuAlNi shape-memory alloy
after continuous casting consisted of the parent $\beta_1$ and $\beta_1'$
martensite phases. The martensite laths have different
orientations into particular grains. The grain size
depends on the place from which the samples are taken.
The grain diameter near to the external surface is higher
than in the center. It was found that the average grain
size was 98.78 μm in particular grains. The temperature
phase transformations determined by DSC measure-
ments were: $M_s = 215 ^\circ C$, $M_f = 169 ^\circ C$, $A_s = 229 ^\circ C$ and $A_f = 191 ^\circ C$. The average hardness of the alloy was 275
HV1.

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