# MICROSTRUCTURE OF Ni40-Ti50-Cu10 SHAPE MEMORY ALLOY STUDIED BY TEM

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# STUDIUM MIKROSTRUKTURY SLITINY Ni40-Ti50-Cu10 POMOCÍ TEM

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**Abstrakt**

Slitina obsahující 40 at. % Ni, 50 at. % Ti and 10 at. % Cu je považována za standardní slitinu s jevem tvarové paměti ze systému Ni-Ti-Cu. Slitiny z tohoto systému jsou vysoce stabilní a korozně odolné. Příprava slitin na bázi Ni-Ti je celkem obtížná v důsledku vysoké reaktivity titanu. Základním předpokladem pro metalurgii těchto progresivních materiálů je striktní dodržení chemického složení připravované slitiny, což je hlavním předpokladem pro získání materiálu s požadovanými transformačními teplotami. Tavení probíhá obvykle při teplotách okolo 1500°C. Pro získání drátu je nejvhodnější užití technologie rotačního překování za tepla v kombinaci s následným tažením. Transformační teploty slitin mohou být měřeny různými technikami, jako jsou DSC nebo DTA, rezistometrickými metodami a v neposlední řadě taktéž deformačními metodami. Pozorování mikrostruktury je možno provádět pomocí světelné optické mikroskopie, ovšem mnohem efektivnější je použití elektronové mikroskopie, ať už SEM či TEM. Experimentální slitina byla připravena ve vakuové indukční peci v grafitovém kelímku a následně byla tvářena a tepelně zpracovávána. Použité vzorky byly ve formě drátu o průměru 2,3 mm. Tento článek je zaměřen na pozorování mikrostruktur slitiny Ni-Ti-Cu po různých typech tepelného zpracování pomocí transmisní elektronové mikroskopie.

**Abstract**

Alloy containing 40 at. % Ni, 50 at. % Ti and 10 at. % Cu is considered to be a standard shape memory Ni-Ti-Cu alloy. These alloys are highly stable and resistant to corrosion. Fabrication of alloys on the base Ni and Ti is quite difficult due to high reactivity of titanium. The basic requirement to metallurgy of these advanced materials is strict adherence to chemical composition of the alloy, which is the main condition for obtaining of the alloy with the required transformation temperatures. Melting operations are usually realised at the temperature of approx. 1500 °C. For obtaining of wire it is the best to use technology of swaging in combination with subsequent drawing. Transformation temperatures measurement should be realised by DSC method (differential scanning calorimetry) or DTA method (differential thermal analysis), by resistometric methods and also by deformation methods. Observation of

microstructure should be realized by optical microscopy, but more effective is use of electron microscopy, such as SEM and TEM respectively. Experimental alloy was prepared in vacuum induction furnace in graphite crucible and then forged and heat treated. The specimens were in the form of wire with diameter 2.3 mm. This article deals with observation of micro-structural characteristics of Ni-Ti-Cu shape memory alloy, after different types of thermal treating by transmission electron microscopy.

**Key words:** Ni-Ti alloys, Transmission electron microscopy, vacuum induction melting

## 1. Introduction

Alloys from the system Ni-Ti-Cu, which are usually prepared by alloying by Cu to the expense of Ni in volumes up to approx. 30 at. %, show shape memory phenomena, similarly as binary Ni-Ti alloys. Addition of Cu also reduces high influence of composition on transformation temperature, transformation hysteresis and flow stress in martensitic state [1]. Amount of added copper also influences significantly manner of transformation. Addition of copper causes forming of martensite B19. In dependence on running transformations in respect to the copper contents the following two cases can occur [2, 3, 4]: 1) if the Cu contents is less than 5 at. % (Fig. 1), there occurs a transformation as in case of binary alloys (Ni-Ti). It means that single stage transformation B2→B19´ occurs. 2) if the Cu contents in the alloy is higher than approx. 7 at. %, (Fig. 1), there occurs high-temperature transformation of B2 phase to martensite B19 and then to martensite B19´. Transformation sequence can be therefore expressed as B2→B19→B19´.

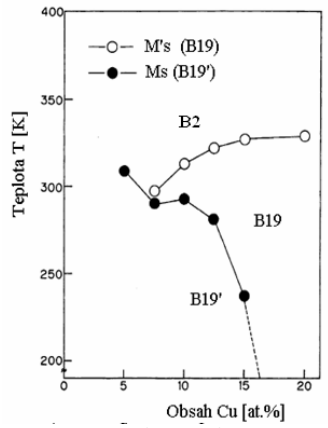


Fig.1 Influence of copper contents on change of areas of occurrence of martensites B19 and B19´[4]

TEM technique makes it possible to combine morphological information obtained from the image, which is formed in light or dark field, with information from diffraction photos taken by the method of selective (SAD) or convergent (CBED) diffraction. It is characteristic for shape memory Ni-Ti-(Me) based alloys, that martensitic phases R, B19 and B19´, formed at cooling of cubic phase B2, have lower crystalline symmetry than initial phase B2. When defined crystallographic relation exists between the parent phase (B2 austenite) and daughter phases (martensite R or B19´), lower symmetry of martensitic crystals leads to a possibility of forming more crystallographic variants of martensite inside one initially austenitic grain. Saburi mentions

existence of four crystallographically equivalent variants for martensite of the type R, six variants of martensite B19 and twelve variants for martensite of the type B19´ [5, 6].

## 2. Experiment

Experimental alloy was prepared by melting in a graphite crucible in high-frequency induction vacuum furnace. Prior to melting the furnace was evacuated and flushed three times with Ar 6N. The alloy was then re-melted in vacuum and cast into a graphite ingot-mould. In this manner a round ingot with diameter of 10 mm and height of 300 mm was obtained. It is necessary to use for preparation of these alloys the purest possible input materials in order to ensure the required quality of the prepared alloy and satisfactorily low contents of gases. In this case the following materials were used: Ni 4N (impurities - C 0.01 %, Fe 0.0048 %, Al < 0.0002 %, Ti 0.0056 %, $O_2$ 0.002 %, $N_2$ 0.0002 %), formed Ti 2N8 (impurities – C 0.025%, Fe 0.016 %, Al < 0.002 %, Ni 0.051 % $O_2$ 0.061 %, $N_2$ 0.0002 %). The charge was also suitably arranged in the crucible, exactly in accordance with the work [7]. In this manner the alloy was prepared with the following contents of undesirable elements: $O_2$ – 0.0548, $N_2$ - 0.0013, C – 0.035 hm. %.

After metallurgical preparation of the alloy it was formed – by combinations of swaging at the temperature of 850°C followed by drawing. A wire with diameter of 2.3 mm was prepared by this technology. Prepared samples of wire (length approx. 60mm) were subjected to various modes of heat treatment. The first stage of heat treatment consisted of homogenisation annealing and cooling in water in the mode 850°C / 30 min. / water. This step was realised in resistance furnace with atmosphere o Ar 4N6. The second step consisted of alloy aging under low pressure at the temperature of 500°C and various durations of dwell in the furnace. Table 1 gives a summary of samples.

Table 1 Summary of samples

| | **Homogenisation annealing** | **Aging** |
|---|---|---|
| **A** | 850°C/0.5 h/ water | 500°C/0.5h |
| **B** | 850°C/0.5 h/water | 500°C/10h |

Samples for TEM were taken from the component volume by electro-spark cutting. Standard holders of TEM foils were designed in such a way that they supported a foil in the form of target with diameter of approx. 3 mm. Cut slices with thickness of approx. 0.6 mm were further thinned by mechanical grinding on metallographic sand papers down to the thickness of approx. 0.15 mm. This operation requires good removal of generated heat, and in case of austenitic foils it is prohibited to use high pressure force of sample to the sand paper in order to prevent forming of the phase B19´ induced by mechanical stress. Great attention at preparation of TEM foil must be paid to thermal mode during handling of the sample. For this reason it is generally more advantageous to choose conditions of subsequent electrolytic thinning of the foil (in the equipment TENUPOL made by Struers) in such a way that temperature of electrolyte during process does not fall below +10°C. These conditions can be fulfilled by use of electrolyte 95% CH3COOH and 5% HClO4. It is necessary to select flow of electrolyte through nozzles in central part of the scale. Flushing of the perforated foil was made in a beaker with distilled water with few drops of ammonia and then in pure ethanol. As a result of this process TEM foils were obtained with sufficiently thin areas for observation of microstructure at acceleration voltage of electrons of 120 and 200 kV.

## 3. Results and discussion

TEM photos in Fig. 2 show microstructure of the samples A and SAD from the zone of carbidic particle delimited by circle selection shutter. With respect to transformation temperatures determined by DSC method for material state A, and with respect to the electrolyte temperature used for preparation of TEM foils it can be assumed that preparation of the TEM foils from the sample A was realised at the temperature close to the value M1f. Share of the phases in the Fig. 2a, where substantial part of microstructure is formed by the phase B19, also corresponds with this fact. Diffraction pattern in the Fig. 2b confirms presence of carbidic particles TiC. Symmetry of diffraction pattern corresponds to the zone of axis of crystallographic planes $[111]_{TiC}$. While presence of carbidic phase in microstructure of the alloy was confirmed, we did not manage to detect in investigated foils an oxidic phase $Ti_4Ni_2O$.

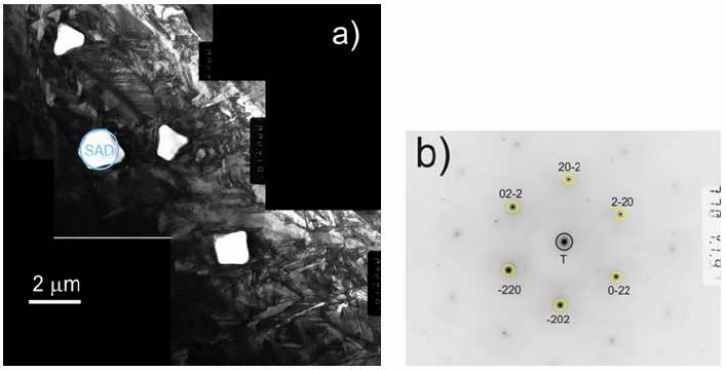


Fig.2 Microstructure of the sample A. (a) TEM of light field with marked position of selective shutter at diffraction analysis of precipitate, (b) corresponding SA diffraction documenting presence of carbidic phase TiC in the matrix of the phase B19 (zone $[111]_{TiC}$)

Small volumetric part of the initial phase B2 found in TEM foils and documented in the Fig. 3 manifests the fact that transformation B2 → B19 is not at the temperature of preparation of the foil and its observation by TEM method completely accomplished yet. As it is evident from the Fig. 3, initial phase B2 contains appreciable density of dislocations, which are probably related to processing of a ternary alloy at its preparation, and it very probably stabilises this phase at thermal mode during preparation and process of TEM observation.

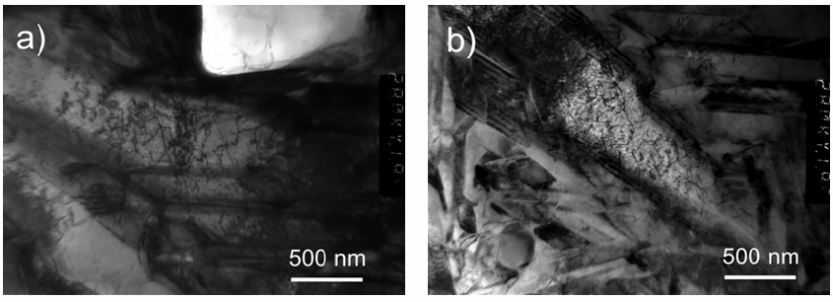


Fig.3 Microstructure of the sample A. (a-b) Dislocation density in residual phase B2 found in majority phase B19

Results that are almost identical with those obtained for the sample A, are presented also for the sample B in the Fig. 4, where the part (a) shows general picture documenting

presence of the phases B19 and B2, and the part (b) shows a detailed view of dislocation structure contained in the residual phase B2 after thermal-mechanical treatment of ternary alloy. In spite of the fact that duration of dwell at the aging temperature differs significantly for the samples A and B, we were unable to determine by TEM method in microstructure of these two material states any substantial differences, we were namely unable to detect any other precipitates of secondary phases.

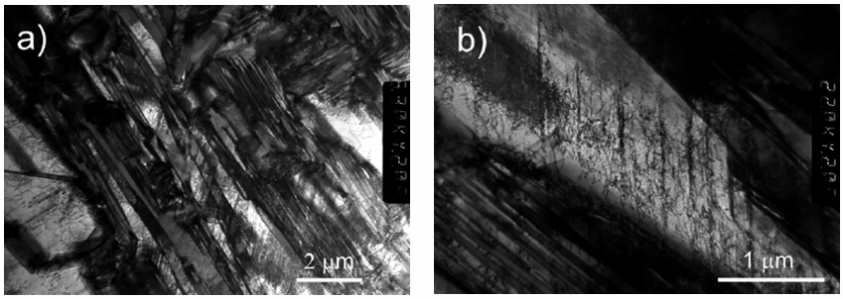


Fig.4 Microstructure of the sample B. (a) Typical arrangement of variants of the phase B19 forming a structure minimising elastic energy of martensite. (b) Dislocation density in residual phase B2 found in the majority phase B19

In the next stage experiments with temperature cycle during TEM observations were performed. TEM foil from the sample B was chosen for these experiments. This foil was inserted into the holder Gatan 636-DH, which enables controlled change of the sample temperature within the interval from –170 to 110°C [8]. Objective of these experiments consisted particularly in initiation of reverse transformation B19 → B2 by heating of the foil, and in an attempt of characterisation of the state of microstructure of austenitic phase B2. Result obtained during heating of the sample is documented in the Fig. 5, where the part (a) shows one grain of polycrystal at the temperature 24.7°C, and the part (b) shows the same grain at the temperature 90.0°C.

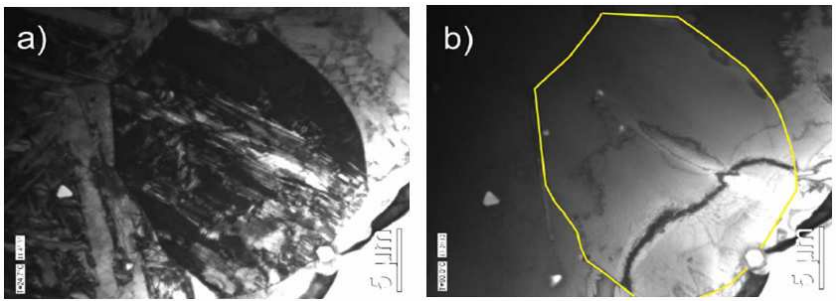


Fig.5 Microstructure of the sample B at the temperatures: (a) 24.7°C and (b) 90.0°C. The same grain is shown during in-situ temperature cycle in TEM before (picture (a)) and after (picture (b)) reverse transformation B19 →B2

Corresponding diffraction pictures presented in the Fig. 6 confirm unequivocally that reverse transformation B19 → B2 occurred in the assumed temperature interval and that microstructure is at the temperature 90°C formed almost uniquely by the phase B2. Further observation realised at the temperature of 90°C proved clearly that in microstructure of ternary alloy no precipitation of phases rich in nickel occurs. However, due to result of artefacts formed

on the surface of TEM foil at relaxation of oxidic layer for direct and reverse martensitic transformation we were unable to ascertain, whether initial phase B2 contains after heat treatment residual dislocation density.

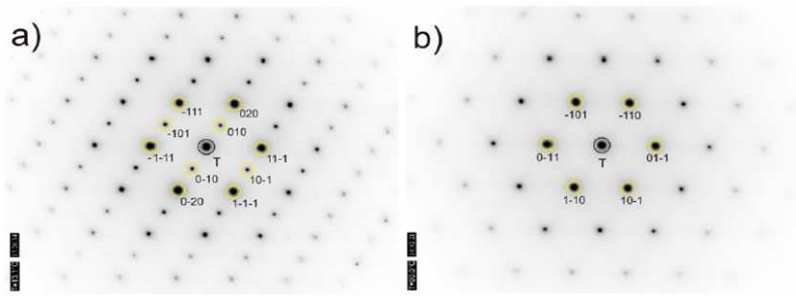


Fig.6 Diffraction patterns taken at the same place of the sample B during in-situ temperature, cycle at TEM with identical inclination of the foil. (a) SAD in the axis of the zone $[101]_{B19}$ at the temperature 13.1°C (it corresponds to the microstructure in the Fig. 4a) and (b) SAD in the axis of the zone $[111]_{B2}$ at the temperature 90.0°C (it corresponds to the microstructure in the 4b)

## 4. Conclusion

Alloy was prepared in the vacuum induction furnace and also wires suitable for subsequent experiments. It was found during investigation of microstructures by TEM methods that carbidic phases are present in the microstructure of investigated samples, which are related to the process of preparation of the alloy in a graphite crucible. No oxidic inclusions of the type $Ti_4Ni_2O$ were found. Comparison of material states A and B showed that in spite of substantial difference of heat treatment of these samples, differences of microstructures are not significant. No other phases are formed here, contrary to the binary Ni-rich system Ni-Ti. The alloy Ni40-Ti50-Cu10 transforms according to the scheme B2→B19→B19´. For the given conditions of preparation and course of TEM observation we succeeded in finding the dominant phase B19 and residual phase B2 stabilised by dislocations.

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