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ВАН МООРЛЕГЕМ ВІЛФРЕД

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РОЗРОБКА ТА ДОСЛІДЖЕННЯ НОВИХ Ni--Ti-СПЛАВІВ З ЕФЕКТОМ ПАМ'ЯТІ ФОРМИ ТА ЇХ ПРАКТИЧНЕ ЗАСТОСУВАННЯ

Спеціальність 01.04.07 -- Фізика твердого тіла

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З дисертацією можна ознайомитись у бібліотеці інституту. Ваш відгук, завірений гербовою печаткою, просимо надіслати за вказаною адресою.

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INSTITUTE OF METAL PHYSICS

VAN MOORLEGHEM WILFRIED

THE INVESTIGATION OF NEW Ni–Ti SHAPE MEMORY ALLOYS WITH EMPHASIS ON THEIR APPLICATION

Speciality 01.04.07 – Solid State Physics

Abstract of the Dissertation Submitted for a Defence
to Receive Ph. D. Degree in Technical Sciences

Kiev—1994

This manuscript is an abstract of the Ph. D. thesis.

The work was implemented at the Institute of Metal Physics, Ukrainian Academy of Sciences, Katholieke Universiteit Leuven, Belgium, and at AMT, Belgium.

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Leading organization: KIEV POLYTECHNIC INSTITUTE

Defence of the thesis will take place 9 Februery 1994 at 14 h. at the meeting of the Specialized Council DO16.37.01 of the Institute of Metal Physics, Academy of Sciences of Ukraine, 36, Vernadsky blvd., 252680 Kiev

One may look through the thesis at the library of the Institute of Metal Physics.

Synopsis of the thesis has been sent 4 January 1994

Scientific Secretary of the Specialized Council

Cand. of Phys. and Math. E. G. MADATOVA

GENERAL CHARACTERISTICS OF THE WORK

The thesis is devoted, mainly, to the development of high temperature Ni—Ti based Shape Memory Alloys.

The aim of the work was to develop a High-Temperature Ni—Ti based Shape Memory Alloy, in particular a Ni—Ti—Zr or a Ni—Ti—Hf based alloy, with M_f temperature above 100 °C, and a reasonable ductility for production reasons. Scientific novelty of the work can be found in the systematic approach, more than 100 alloy compositions were studied to obtain a high temperature and ductile Shape Memory Alloy with good Shape Memory performance.

Due to the scale up of the work to a commercial production level, the practical value of the work is evident.

Main scientific propositions to be defended:

A REVERSIBLE MARTENSITE SYSTEM WHICH WAS STABLE UP TO HIGHER TEMPERATURES AS HIGH AS 200 °C IN COMBINATION WITH A NECESSARY DUCTILITY AND A TWO WAY SHAPE MEMORY EFFECT (2.5 %) UNDER LOAD IS DESCRIBED.

Personal contribution of the author can be found:

— on the technical side e. g. Vacuum induction casting, extrusion, swaging, rolling, wire drawing,

— on the scientific side e. g. evaluation of the alloys by Differential Scanning Calorimetry (DSC), Light microscopy, SEM, Shape Memory measurements, research strategy,

— on the practical applied side by defining actual high temperature Shape Memory Alloy requirements out of the industry for a possible later commercializing.

Approbation of the work.

Research results were presented at following conferences:

— Shape Memory Alloy Conference, Michigan State University, 15—17 August 1988

— The MRS international Meeting on Advanced Materials, Tokyo, 1988

— The 3rd International Conference on New Actuators, Bremen, 1992

— The 4th International Conference on Space Structures, University of Surrey, 1993

— EEC-COMETT 87/2/C-2/00863, Barcelona, 1989
— Studiedag Nieuwe Materialen, Kortrijk, 1987
— Formgedachtnislegierungen, Technische Akademie Esslingen, 1993
— MRS international Meeting on Advanced Materials, Tokyo, 1993
— The International Conference on Shape Memory and Superelasticity: Engineering and Biomedical Applications, Asilomar, to be held in 1994
— The 4th International Conference on New Actuators, Bremen, to be held in 1994

Publications:
There were published nine papers on the theme of the thesis.

SYNOPSIS OF THE THESIS

In chapter one, the introduction, based on the literature the definitions of the one-way and two-way Shape Memory and other associated phenomena (superelasticity, superplasticity, high damping capacity etc.) are given along with critical discussion of their nature. Necessary conditions for Shape Memory manifestation in any material were determined to be:
— martensite transformation, specifically a thermoelastic martensite (Kurdumov's effect);
— martensite transformation should be crystallographically reversible;
— parent and martensite phases should be ordered;
— deformation in the martensite state should be accommodated by reorientation of its variants.

It is admitted that the transformation temperatures, the hysteresis and the reversible macroscopic strain are dependent presumably on the chemical composition of the alloy. Besides they are dependent on the thermomechanical treatment and on the exploitation conditions (e. g. number of the temperature cycles through martensite transformation onset under external stress or without it).

The actual need of the industry is mentioned, following which THE MAIN GOAL of this thesis
— THE DEVELOPMENT OF A HIGH TEMPERATURE SHAPE MEMORY ALLOY WITH A M_f TEMPERATURE ABOVE 100 °C.

The request from the industry is due to possible high environment temperatures of actuators. An example is the automatic circuit breaker where the activation is normally about 150 °C. Other possible applications are situated in the automotive industry, because the temperature in a car can rise up to about 100 °C due to direct radiative heating of the sun.

Keeping in mind the practical aspect for a later possible commercial production, TWO MINOR GOALS WERE DEFINED:

— A MINIMUM DUCTILITY which is required for production reasons, so normal production techniques such as rolling can be applied.

— A MINIMUM, STABLE, SHAPE MEMORY EFFECT OF 1.5 %.

Initially Ni—Ti—Zr and later Ni—Ti—Hf were chosen for investigation, the first choice following the literature and the second due to the chemical similarity of Hf and Zr.

In chapter two «The influence of ternary elements on the martensite transformation in Ni—Ti systems» a review of the literature is done taking into account production reasons. Main achievements and general conclusions are summarized below:

— No alloy, as mentioned in the goals, is industrially available.

— Interpreting the literature on this topic, there appears to be a lack of coherence. The main problem here is that authors do not clearly specify their treatments and measuring procedures and contradictory data are reported. A standard for Shape Memory measurements and treatments will help interpreting the literature and increase the interchangeability of data.

Due to the lack of missing information in regard to the actual state, a research strategy was set up to achieve the goals without the need of casting too many different alloys.

— Potential candidates as ternary components may be Al, Ga, Hf, In, Os, Re, Ru, Zr as substituted for Ti and Au, Co, Cu, Fe, Pt, Nb as substituted for Ni.

— To satisfy the request of the main goal of the thesis a number of candidates should be narrowed to Cu for the first step, and Zr and Hf (as isoelectronic to Ti) to continue development of Shape Memory Alloys the most practical for industrial manufacturing.

The novel result of this research was a systematic overview of the Ni—Ti—Zr system in the range of interest from a Shape Memory point of view.

Replacing the Zr by Hf a further increase in transformation temperature, up to 250 °C, and a stable two way Shape Memory, up to nearly 3 %, was achieved.

The third chapter is devoted to the Ni—Ti—Cu system.

This interesting system has a better long-term stability, a smaller hysteresis and a lower sensitivity of the transformation temperature to changes in composition.

Keeping in mind the main goal and taking into consideration the literature data on variation of the transformation temperatures with composition in ternary TiNiCu system the alloys with content of $(7 \div 8.3)$at.%Cu—$(49.5 \div 51.5)$at.%Ti—Ni were chosen for investigation. Alloy preparation was as follows: melting in vacuum induction furnace in the form of cylindrical ingots ($d = 20$ mm, $l = 100$ mm) followed by hot rolling at 900°C (into strips of 2 mm thickness).

Transformation temperatures were determined by calorimetric measurements and bending technique.

Microstructure studies show presence of large number of precipitations which were identified as $Ti_2(Ni,Cu)$ by microprobe analysis. Volume fraction of those precipitations increases with Ti content. Transformation temperatures do not increase with Ti due to its removing from the matrix. Since Ti_2Cu is a brittle phase that decomposes at 984 °C so the alloys with higher Ti-content are very brittle.

In view of later serial production, memory wires of a NiTiCu alloy AMT07020 (48.8%Ni—45.2%Ti—6.0%Cu) were chosen and the following manufacturing steps were examined:

- cold wire-drawing
- final heat treatment of the wire
- inducing the memory effect
- quality control.

To differentiate material behavior during varying the process conditions mentioned above the parameter $\beta = \varepsilon_0/\varepsilon_{max}$ (ratio of the plastic deformation ε_0 to the (elastic + plastic) deformation ε_{max}) was used.

Based on variations of β with annealing temperature and holding time the recrystallization state of the finally annealed memory wire was determined to be 400 °C, 15 minutes.

Annealing a wire at higher temperatures (500 °C) gives a creep of ca. 2.5 % at a shape memory strain ca. 4.1 % after 1000 thermal cycles. For lower annealing temperatures the material does not creep but Shape Memory is smaller (~ 1.6 %).

So, in this chapter the thermomechanical treatment for this alloy was optimized as a function of:

- Shape Memory strain
- Recovery stress
- Creep

It was found that a deformation ratio of 30 %, annealing at 400 °C for 15 minutes followed by a water quench and a prestrain (deformation in the martensitic state) assures a stable Shape Memory effect. As an optimal compromise a wire was made with the following characteristics: Shape Memory effect 4 %; Creep 0.3 %; β value 0.685.

The fourth, fifth, sixth and seventh chapters present the results of the research done on the Ni—Ti—Zr system respectively concerning with alloys of lower Zr content, higher Zr content, high Zr content with optimization of the Ni content and a Ni—Ti—Zr pilot casting respectively.

Comparison of Ti—Ni and Zr—Ni phase diagrams is done. Both Ni-base and Zr-base phases have small existence range but additional phases should be taken into account for intermediate composition.

Preparation of the alloys under study:

— for low Zr content each samples were remelted four times to improve the homogeneity, a vacuum induction furnace was used.

— for higher Zr content melting was made under Ar atmosphere.

It was found out that in ternary TiNi—Zr alloys precipitations of $(Ti,Zr)_2Ni$ phase are observed in large amounts. Distribution of the basic components is such that matrix is depleted in Ti but Zr is equally partitioned between the precipitate and the matrix.

The experiments showed that up to 2.7at.% Ti can be substituted for Zr without a change in the transformation temperature.

For higher Zr-content (up to 20at.%) the transformation temperatures vary as shown in Fig. 1.

A_s and A_f increase with increasing Zr-content till $A_s = 122$°C. M_s and M_f show a minimum. The values do not show a significant dependence on the Ni-content.

At small Zr-content (3 at. %), the change of the transformation temperatures A_s and A_f with the Zr-content is negligible.

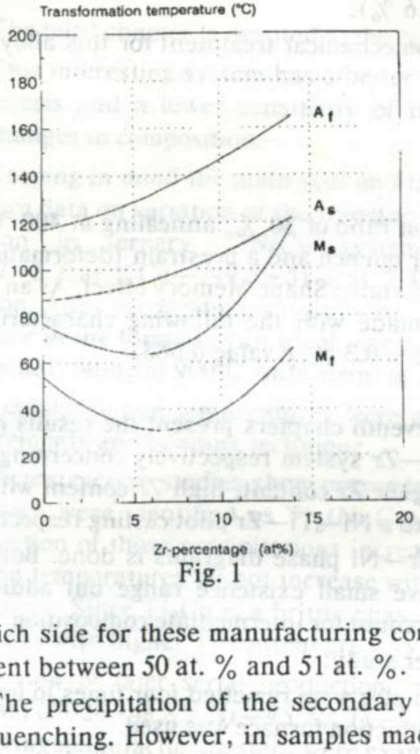

Fig. 1

Till 7 at. % Zr, M_s and M_f temperatures decrease. Due to this effect the hysteresis of the alloys first increases and then at higher Zr-content of the alloys, decreases again.

The microstructure of the alloys with Ni deficiency is marked by a dendritic precipitation of a secondary phase. The precipitate has a composition comparable to $(Ti,Zr)_2Ni$ (as measured by EDX-analysis). In the matrix, which enriches itself with Ni as a result of precipitates rich in Ti and Zr, there is extra segregation of Zr in vicinity of the precipitates.

The phase boundary of the single phase (Ti,Zr)Ni on the Ti rich side for these manufacturing conditions lies at a constant Ni-content between 50 at. % and 51 at. %.

The precipitation of the secondary phase can not be suppressed by quenching. However, in samples made by meltspinning they are more finely distributed.

The structure of alloy with a higher Ti-content is like above, though the size of the precipitates is smaller, as well as the volume fraction.

This results in better mechanical properties.

In chapter six «High Zr containing Ni—Ti alloys with optimum Ni-content», based on the experimental data obtained in previous chapter, the alloys were chosen with Zr-content varying in the range $5 \div 35$ at. % in order to define the optimum Ni-content for a given Zr fraction. The composition was close to the stoichiometric intermetallic NiTi system.

Other Ni-rich phases are observed in addition to $(Ti,Zr)_2Ni$ phase when the Ni-content is above the solubility range (from 50 at. % to 51 at. %).

Both the Ti-rich as well as the Ni-rich phases are surrounded by Zr enriched zones.

Electron microscopy investigation showed a fine martensite with coherent martensite—martensite variant boundaries.

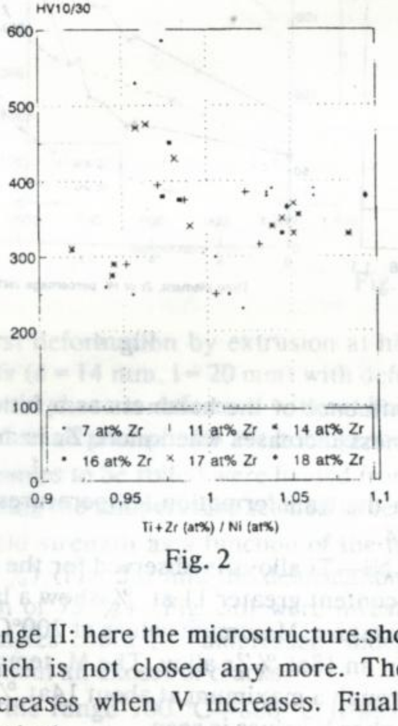

Fig. 2

The Vickers hardness as a function of the composition ratio V (V = (Ti + Zr)/Ni) is presented in Fig. 2.

Three ranges can be distinguished.

For $V < 0.96$, the hardness decreases when V increase.

The next range, up to $V = 1.01$, starts with an initial doubling of the hardness followed by a decrease to the original values.

In the last range, $V > 1.01$, the hardness increases continuously.

Range I: here the microstructure shows Ni rich precipitates, simultaneously with the Ni-rich network phase which is in this range a closed network.

Range II: here the microstructure shows only the Ni rich network phase which is not closed any more. The volume fraction of the network decreases when V increases. Finally it vanishes when range III is reached.

Range III: here the microstructure shows only $(Ti,Zr)_2Ni$ precipitates. Their volume fraction increases with V.

Since the network phase can disappear after annealing, range II corresponds to the solution range in the phase diagram. Ranges I and II are the two phase regions on the Ni side and the (Ti + Zr) side of the phase diagram. It is clear that in these two regions the hardness will increase when a higher volume fraction of precipitates is established.

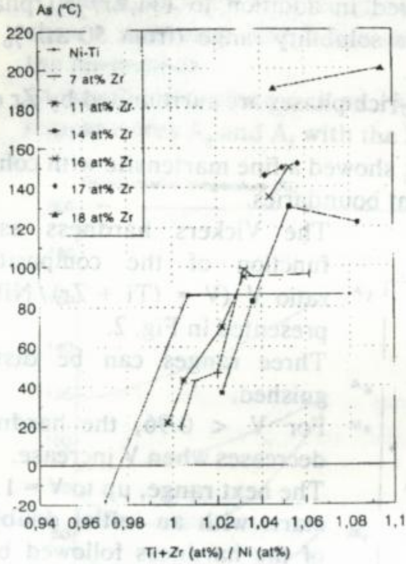

Fig. 3

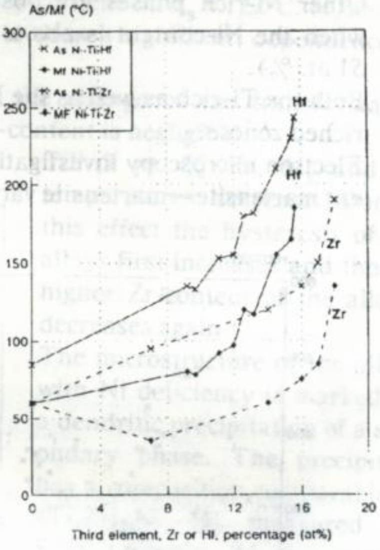

Fig. 4

Only in range III we see an influence of the hardness as a function of the Zr-content; here the hardness increases when more Zr is added to the alloy.

The influence of Ti and Zr on the transformation temperatures in this system is shown in Figs 3 and 4.

The same tendency as for the Ni—Ti alloys is observed for the Zr containing alloys. Alloys with Zr-content greater 11 at. % show a large increase in transformation temperature. Maximum values of 200°C for the A_s temperature were reached in an 18at. % Zr alloy. The M_f temperature increases also after passing through a maximum at about 14at. % Zr.

A clear shift of the curves to higher V values is seen.

The reason for this is that higher volume fractions of ZrO_2 were formed for higher Zr containing alloys. This means that the real V value in the matrix is lower.

Chapter seven «Ni—Ti—Zr pilot casting» presents the results of semi-industrial production of 35 kg Ni—Ti—Zr ingots prepared in a high vacuum induction furnace. Two alloys were melted namely AMT7612 (16 at. % Zr) and AMT7611 (17.5at. % Zr).

Technological steps were as follows:

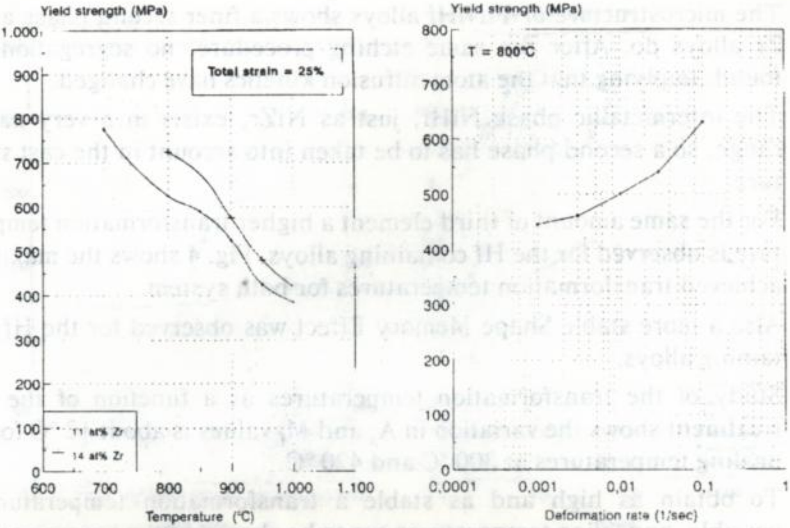

Fig. 5

First deformation by extrusion at high temperatures of cylindrical ingots (d = 14 mm, l = 20 mm) with deformation ratio 4.6. On this step the brittle phase is deformed without being interrupted into different parts and small precipitates are homogeneously distributed in the matrix.

Samples to be rolled were heated from 700 °C up to 1000 °C. During hot rolling the temperature seemed to be crucial parameter.

Yield strength as a function of the test temperature (for total strain of 25 %) (Fig. 5a) and the deformation rate (at 800 °C for total deformation of 75 %) (Fig. 5b) were investigated by compression tests. The samples could be compressed, independent on the deformation rate, without an excess of cracks.

In the range 700 °C—800 °C it was possible to obtain more passes a total reduction of 50 %. A pronounced one way Shape Memory Effect of up to 3 % was found.

In the eighth chapter the Ni—Ti—Hf system is presented.

Zr and Hf from a chemical point of view are quite similar. In nature, they are also found together. So one can expect that Hf will have about the same influence on the transformation temperature, microstructure and Shape Memory Effect as Zr has, when it is added to the binary Ni—Ti system.

The microstructure of TiNiHf alloys shows a finer second phase as the Zr alloys do. After the same etching procedure, no segregation was found, implying that the atom diffusion kinetics have changed.

The intermetallic phase NiHf, just as NiZr, exists in a very narrow range, so a second phase has to be taken into account in the cast structure.

For the same amount of third element a higher transformation temperature is observed for the Hf containing alloys. Fig. 4 shows the maximum achieved transformation temperatures for both system.

Also a more stable Shape Memory Effect was observed for the Hf containing alloys.

Study of the transformation temperatures as a function of the heat treatment shows the variation in A_s and M_f values is about 12 °C for annealing temperatures at 300 °C and 420 °C.

To obtain as high and as stable a transformation temperature as possible, annealing temperatures are to be chosen in the lower range.

Intensive studies of Shape Memory behavior under stress and different heat treatments show that there are distinct temperature range and holding time to reach relatively high value of two-way Shape Memory Effect.

Fig. 6 shows the quite remarkable independence of the applied stress on the transformation temperature. The same figure shows that a two-way Shape Memory Effect of nearly 3 % can be reached after a training of 350 thermomechanical cycles. The two-way Shape Memory Effect as a function of the applied stress for different Hf-content increases up to 2.5 ÷ 3 % for stresses up to 350 MPa.

A more ductile structure was created after a full annealing at 1200 °C. It was observed this treatment alters the morphology of precipitates at the grain boundaries.

Fig. 7 shows the influence of different heat treatments on the two-way Shape Memory Effect as a function of cycling (stability).

Thus, the transformation temperature for Hf containing alloys are higher compared with the alloys modified with Zr; also the transformation temperatures are more stable for the Hf containing alloys and show a smaller stress dependency; thermal treatment can best be chosen in the lower temperature range. An addition of 5.8 at. % Cu decreases the transformation temperatures drastically.

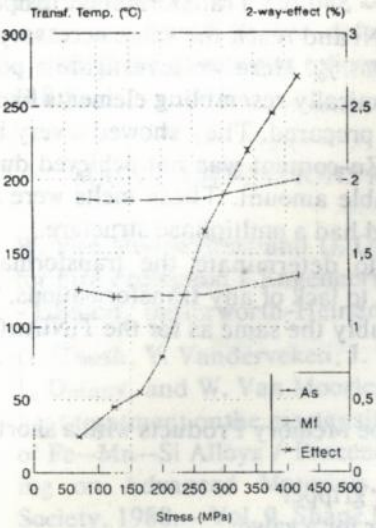

Fig. 6

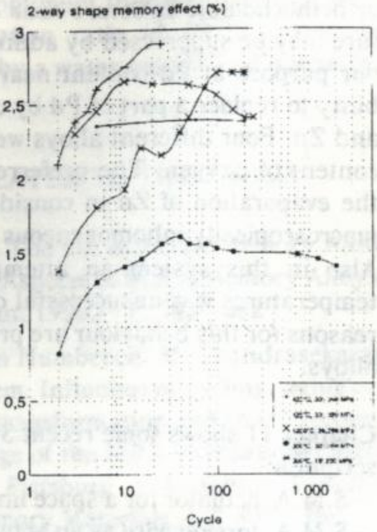

Fig. 7

Chapter nine «Ni—Ti—Au system» details the attempt to replace gold by copper in the Ni—Ti—Au system.

Copper was tried because it is the only *3d* element that does not decrease M_s temperature (V, Cr, Mn, Fe and Co decrease the transformation temperature). Because Au is situated in the same group of the Periodic Table due to Mendeleyev, an attempt was made to replace partially Au by Cu in Ni— Ti—Au system due to the high price of gold and the important solubility of Au in Ni—Ti system. Four alloys with nominal content of Ti near 50 at. % were prepared by the technique mentioned above.

No sample could be made that showed a Shape Memory Effect, probably due to the high oxygen content. We may assume that the variety of different phases and their high volume fraction are able to suppress the martensite transformation in the matrix.

Future work will be dedicated to replace Cu by the chemically similar element Zn.

In chapter 10 «Ni—Ti—Pd system» a similar attempt, to achieve our goals, is described for the Ni—Ti—Pd system.

As it is known the intermetallic compound 50Ti—50Pd has an ordered CsCl structure which undergo martensitic transformation to monoclinic

or orthorhombic structure near $M_s = 540$ °C. Transformation temperature may be suppressed by adding Ni and reach the value necessary for our purpose at Pd-content near 20at.%. Here we investigate a possibility to replace a part of Pd by chemically resembling elements like Cu and Zn. Four different alloys were prepared. They showed a very high content of oxygen. The preferred Zn-content was not achieved due to the evaporation of Zn in considerable amount. These melts were also macroscopically inhomogeneous and had a multiphase structure.
Also in this system an attempt to determinate the transformation temperatures was unsuccessful due to lack of any transformations. The reasons for this behaviour are probably the same as for the TiNiAu(Cu) alloys.

Chapter 11 shows some recent Shape Memory Products with a short description:

-- S.M.A. actuator for a space linear gripper
-- S.M.A. torsion wire as an actuator for a valve
-- S.M.A. wire (100 μ diameter) used as the driving element in points of miniature railway models
-- S.M.A. driven open mechanism of an antenna
-- Louvre mechanism actuated by a Shape Memory Spring.

MAIN RESULTS AND CONCLUSIONS

1. The new Ti--Ni-base Shape Memory Alloy containing 17 at. % Hf which demonstrates high transformation temperature ($M_f \sim 200$ °C), two-way Shape Memory Effect with recoverable strain of 2.5 % and advaced physical and mechanical properties was developed.
2. A new technological procedure for producing industrially acceptable Ni--Ti--Zr and Ni--Ti--Hf Shape Memory Alloys with optimum exploitation parameters are proposed.
3. The transformation temperatures for Hf containing alloys are higher compared to the Zr containing alloys.
4. The transformation temperatures for Hf containing alloys are more stable and demonstrate smaller stress dependent than for Zr containing alloys.

5. For the Ni—Ti—Cu system, the optimum thermomechanical treatment was found to be: deformation ratio of 30 %, annealing at 400 °C for 15 minutes followed by a water quench and a prestrain of 8 %.

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