GOLD 2006 PRESENTATION

Gold with a Martensitic Transformation: Which Opportunities?

Stefano Besseghini[1]*,
Francesca Passaretti[1], Elena Villa[1],
Paolo Fabbro[2], Franca Ricciardi[2]

[1] CNR-IENI Dept. of Lecco, Lecco, 23900, Italy Corso Promessi Sposi, 23900 Lecco
[2] UNOAERRE spa, Arezzo, 52100, Italy
* Corresponding author. Tel: +39 0341 499181, Fax: +39 0341 499214 and E-mail: s.besseghini@ieni.cnr.it

Abstract

In this paper we will consider an overview of the precious alloys that could be of interest due to the inherent properties of the thermoelastic martensitic transformation that they exhibit. For sure one of the main representatives of these materials can be considered the AuAlCu system (and the related well known Spangold™). Actually in the literature, since the late '70s, other systems have been indicated of interest but they knew a very limited success. We refer here to some pioneering work from G.B. Brook In more recent time the increasing experience in the science and technology of conventional shape memory alloys like NiTi (which in the meantime successfully reached the application field) brought a new interest for a clear understanding of the potential of these gold alloys. Here we report on results obtained in the three areas: spangold-like alloys, AuCuZn alloys, and a ternary modification of NiTi, i.e. NiTiAu. The samples used for the investigation have been prepared starting from pure metals and thoroughly investigated by means on differential scanning calorimetry, X-ray diffraction at different temperatures and optical microscopy. When possible the samples were submitted to simple recovery test to verify the amount of shape memory and/or pseudoelastic properties.

Introduction

Even if their knowledge cannot be considered widely spread, shape memory alloys (SMAs), definitely left the research laboratories entering the application filed since the beginning of the '90s. This is particularly true for NiTi which is now recognized as the prototype of shape memory alloys due to their large recovery strains (up to 8%), recovery stress (up to 300Mpa) and, last but not least, its biocompatibility which allowed access to the biomedical field. A very complete review on physical metallurgy of Ti-Ni SMA can be found in [1]. The unusual mechanical properties of SMA such as shape memory effect and pseudoelasticity are due to the presence in the material of a thermoelastic martensitic transformation (TMT). It can be activated by temperature modifications or by increasing stress levels thus conferring the above reported properties.

It would be of interest for many applications to have similarly a gold alloy, which can exhibit such solid-state transformation and eventually the same unusual mechanical properties. Some articles are present in the open literature tangling this problem but, apparently, none of the proposed systems knew great fortune. A possible explanation to this aspect can be related to the fact that the physical metallurgy of these alloys is not a simple one; the systems are often intermetallic in nature and prone to exist only in metastable states.

Basically the papers dealing with gold alloys (thus not considering here all the existing work done on Pt and Pd systems) are related to AuCuZn and AuCuAl, the first one can be considered as a relatively straightforward modification of a well-known martensitically transforming alloy such as CuZn. Anyway after some pioneering work by G.B. Brooks [2,3] as early as in 1975 the AuCuZn received small attention apart from the dental applications. In this case it was also proposed the use of the shape memory effect [4-10]. Large part of the investigations was devoted to its transformation properties and the presence of pre-martensitic effects. It has been recognized the presence of a complex sequence of phase transformation from a stable ordered cubic phase at high temperature. According to the composition of interest reported in [3] the B2 high temperature phase transforms to an orthorhombic (τ_3) and monoclinic (τ_4) structure. We investigated the compositions $Au_{22}Cu_{33}Zn_{45}$at%, $Au_{26}Cu_{29}Zn_{45}$at% and $Au_{27}Cu_{28}Zn_{45}$at%. They have a constant Zn content and should coincide with the maximum modification of the transformation temperatures as a function of the composition.

The other system which knew quite attention is the ternary AuCuAl. In this system the surface relieves generated by the martensitic product phase as a special finishing of the surface [11]. The commercial name of this alloys family is Spangold and the prototype system is $Au_{43}Cu_{31}Al_{25}$at%. In spite of a relatively small commercial fortune it deserved scientific focus due to some debate related to the structure of the martensite and to the effect of aging procedure in the parent

Table 1

Summary of the calorimetric characterization performed on AuCuZn samples

	Au22Cu33Zn45 at%							
	Ms	**Mp**	**Mf**	**ΔH**	**As**	**Ap**	**Af**	**ΔH**
	°C	°C	°C	J/g	°C	°C	°C	J/g
S28/06 As Cast	16.0	15.2	13.3	-3.5	18.0	19.7	20.7	4.0
S28/06B Remelted	23.5	21.1	18.2	-3.2	25.4	27.5	29.7	4.0

	Au27Cu28Zn45 at%							
	Ms	**Mp**	**Mf**	**ΔH**	**As**	**Ap**	**Af**	**ΔH**
	°C	°C	°C	J/g	°C	°C	°C	J/g
S29/06 As Cast	59.4	58.5	56.5	-1.50	75	77.1	78.7	1.10
S29/06B Remelted	61.2	58.6	56.4	-3.50	77.1	80.2	82.3	3.30
S29/06C Hot worked	65.4	58.7	45	-1.30	60.1	75.9	89.2	1.20

	Au26Cu29Zn45 at%							
	Ms	**Mp**	**Mf**	**ΔH**	**As**	**Ap**	**Af**	**ΔH**
	°C	°C	°C	J/g	°C	°C	°C	J/g
S30/06 As Cast	-0.5	-3	-6.1	-3.8	1.8	4.1	6.1	3.6
S30/06B Remelted	1.5	0.5	-2	-2.7	2.7	4	5.3	2.9
S230/06C Hot worked	5.2	-7.9	-31.6	-1.9	-17.6	1.3	20.2	2

Ms – Martensite Start temperature
Mp – Martensite Peak temperature
As – Austenite Start temperature
Ap – Austenite Peak temperature
Mf – Martensite Finish temperature
ΔH – Enthalpy of the transformation
Af – Austenite Finish temperature
ΔH – Enthalpy of the transformation

phase on the transformation sequence [12-14]. On this system we investigated the effect of thermal stabilization of the martensite which is known to induce important differences in many SMAs. It was concluded that in the case of Spangold for the investigated composition this effect is negligible. A vacancy movement mechanism is anyway present but is practically impossible to understand from calorimetric measurements which atom species moves. [15] These results being reported elsewhere we will not focus on them in this paper.

In undergoing this investigation we wondered if the binary NiTi system could withstand a ternary substitution of Au yet preserving the transformation properties. It is known that the binary AuTi has many similarities with NiTi transforming from an high temperature B2 austenite to a B19 orthorhombic martensite [16]. Transformation temperatures should be well above room temperature (according to [17] Ms respectively at 440°C and 610°C for the $Ni_{40}Ti_{50}Au_{10}$) thus suggesting some difficulties in real use of the effect. [18]. We investigated both the substitution of Ni for Au and of both Ni and Ti for Au in compositions that are close to 9, 14 and 18Kt gold.

Experimental

All the alloys have been prepared starting from pure metals. AuCuZn was prepared using a special device inserted in a conventional induction melting machine for investment casting (Aseg-Galloni VCM III). The need to modify the melting procedure is basically related to the exceptionally high level of Zn (45at%). This led to two major improvement, from one side a master alloy of CuZn was used to minimize weight loss during melting, from the other side the melting procedure was performed in a sealed, Ar filled quartz tube with a special but simple shape. This prevented vapor evolution from the melt to a major extent. Once melted and thoroughly mixed by mechanically stirring the quartz tube the tube itself was removed from the furnace and placed in a static electric furnace at 600°C where the solidification procedure took place along with a solubilization process. This led to a high degree of homogeneity in the bulk, as proven by EDS analysis, in spite of a massive grain growth and consequent brittleness (Figure 1). According to this procedure three ingots were prepared with the composition reported in the ternary

Figure 1

A prototype of the AuCuZn ingots after furnace cooling spontaneously broken at the grain boundaries

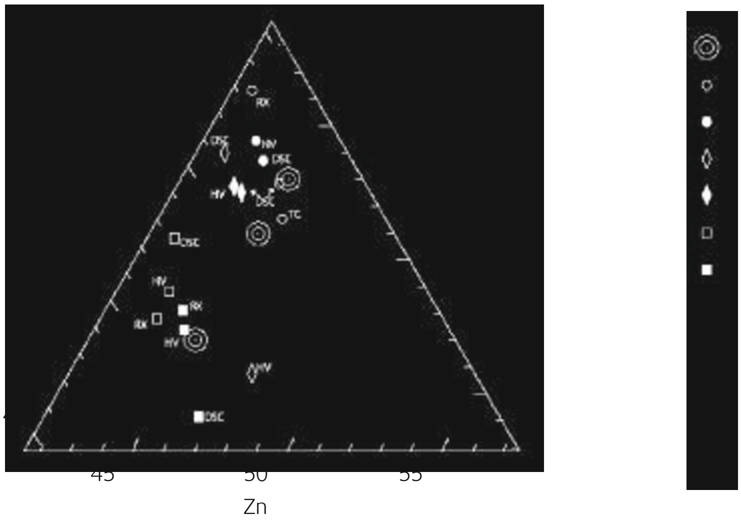

Figure 2

Ternary diagram of the investigated compositions in the AuCuZn system. The major circles show the expected nominal composition, the small symbols, according to the reported legend, the composition checked by EDS analysis on the various samples used for the characterization. See text for details on nomenclature

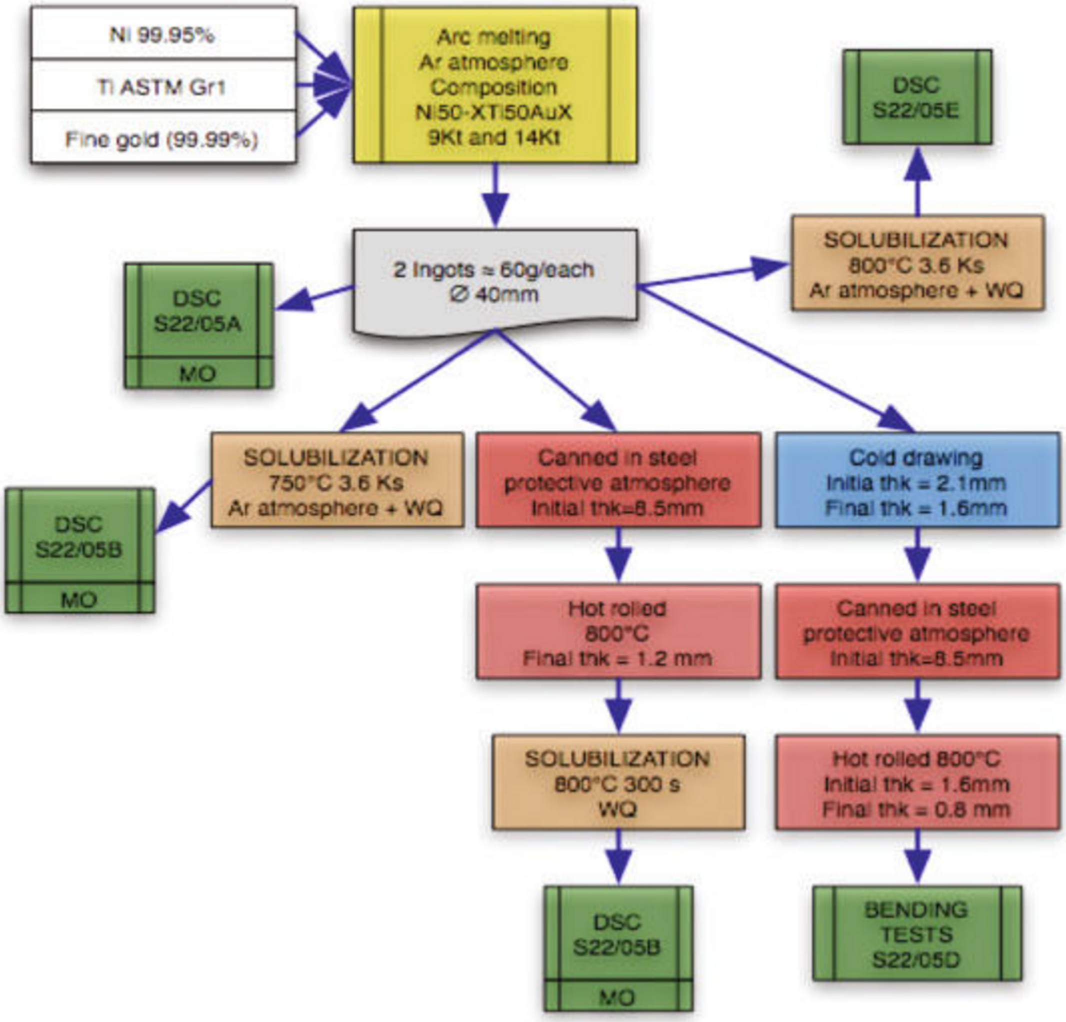

Figure 3

Diagram of the processing route used for the production of the NiTiAu samples reported in the paper

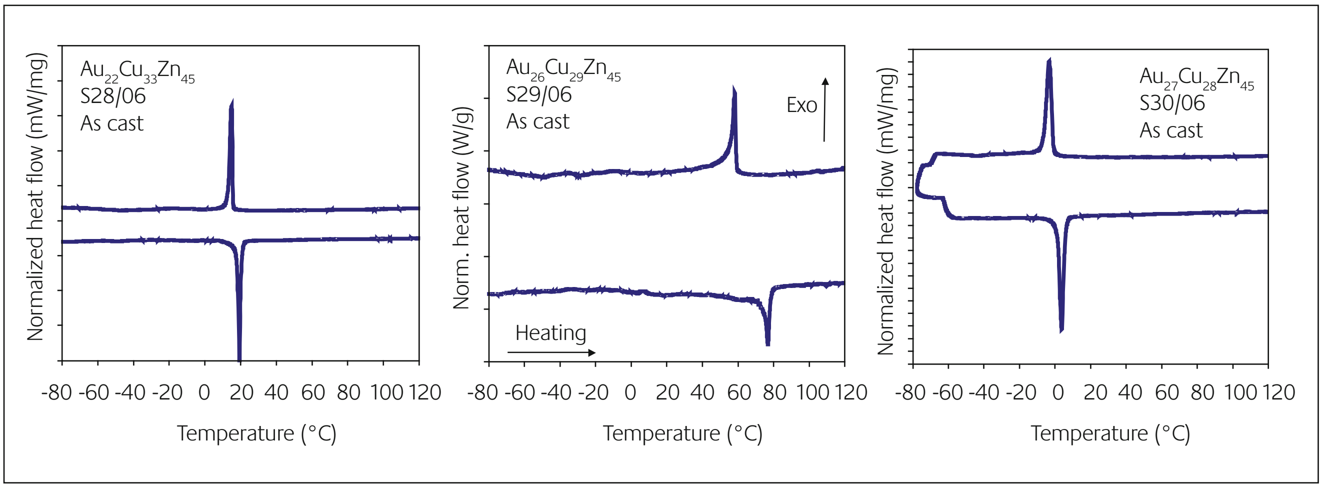

Figure 4

Comparison of the thermograms for the first complete cycle in AuCuZn alloys investigated. Please note the very low hysteresis and strong modification in the transformation peaks

diagram of Figure 2. Due to the impossibility to process ingots with such large grains the same ingot was again inserted in the quartz tube, quickly remelted and quenched in water. The samples named as "B" are those that were submitted to this procedure. The compositions prepared were: $Au_{22}Cu_{33}Zn_{45}$at% (S28/06), $Au_{26}Cu_{29}Zn_{45}$at% (S29/06) and $Au_{27}Cu_{28}Zn_{45}$at% (S30/06). An attempt was made of producing small wires by hot working the alloy. It was possible to obtain small rods of 2 x 2mm^2 and 4 x 4mm^2 that were characterized by DSC.

NiTiAu: due to high reactivity of Ti processing of this alloy in conventional melting machine can be difficult. The alloys were melted in a non-consumable electrode arc furnace in Ar atmosphere (fluxing, 150mbar average pressure). Ingots of about 60g, 40mm in diameter were produced by subsequent melting. After each melting the ingot was turned upside down to increase alloy homogeneity. Alloy compositions were ($Ni_{36.2}Ti_{50}Au_{13.8}$ at% and $Ni_{23}Ti_{50}Au_{27}$ at%). Samples were cut from the ingots, by low speed diamond saw, for calorimetric investigation and for subsequent plastic deformation of the alloy. The whole (and quite complex) set of thermal treatments, hot and cold rolling is summarized in Figure 3. As we succeeded in producing small slab (5 x 50 x 0.5mm^3) of the $Ni_{36.2}Ti_{50}Au_{13.8}$ alloy a memory recovery experiment was performed by bending the slab around mandrels of decreasing diameter and evaluating shape recovery. As the maximum strain applied to the external fiber of the deformed slab is ε_{max}= 2t/(2R + t) being "t" the slab thickness and R the curvature radius of the deforming mandrel.

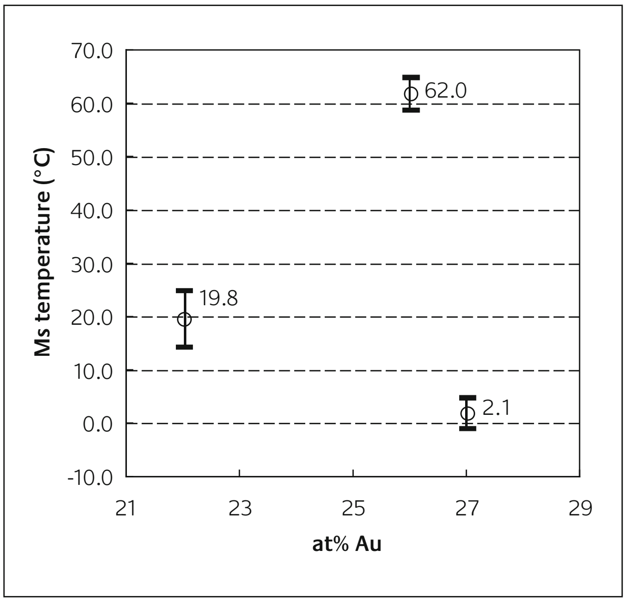

Figure 5

Average values of the Ms temperature recorded on the samples investigated. Error bars are calculated on each set of samples as one time the standard deviation

Characterization of the various samples was performed by means of Differential Scanning Calorimetry (DSC) using a Seiko DSC 220C calibrated with the melting temperature of pure metals (In, Hg). The scanning rate was 5°C/min.

Microstructure characterization was performed by optical microscopy after mechanically polishing and chemically etching the samples. Etchant used was a typical one for NiTi (HNO_3 47vol%; HF 3%vol; H_2O 50%vol). It was applied by gently swabbing the surface of the samples. It allowed to appreciate the general microstructure but a specific etchant should be identified.

Results

AuCuZn

Figure 4 summarizes the calorimetric curves obtained on three samples taken from the as cast alloys. The following Table 1 shows all the relevant transformation parameters of the samples, i.e. the transformation temperatures and the transformation enthalpy both of the direct and reverse transformation. There is a single peak in the entire sample, which is very sensitive to stoichiometric composition.

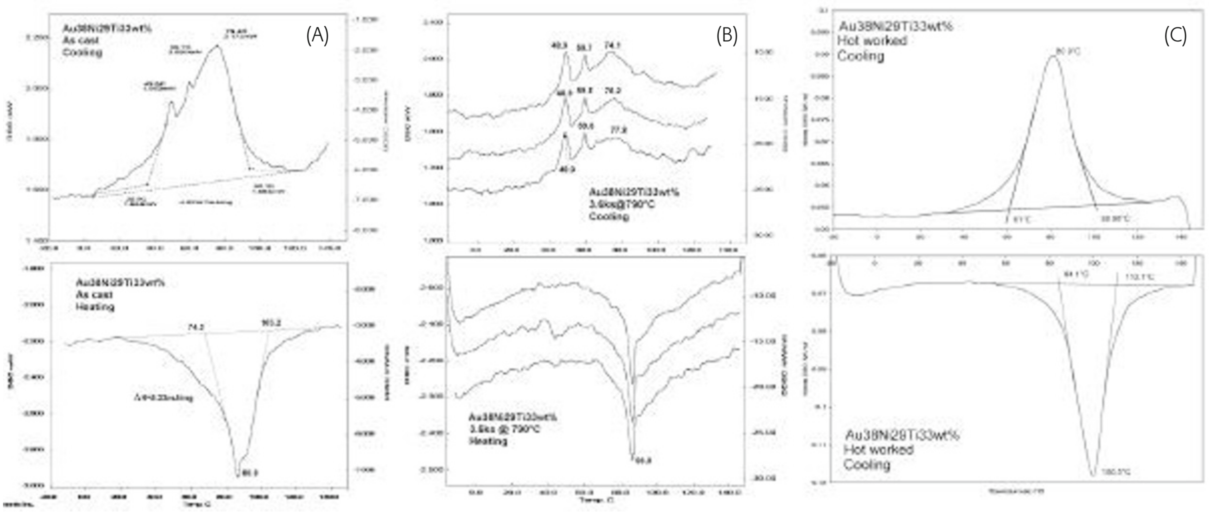

Figure 6

(a) a complete thermal cycle for the $Ni_{36.2}Ti_{50}Au_{13.8}$ *alloy in the as cast state. Main transformation parameters are reported. (b) similar results for the sample annealed for 1 hour at 750°C. The curves refer to three subsequent cycles and are shifted on the y- scale. (c) the same result for the sample annealed at 800°C. Note that the y-axis is not equal. All the curves have been scaled to allow better understanding of the details*

Changing the Au content from 22 to 26at% rises Ms temperature of 40°C but a further increase of only 1at% decreases it by roughly 60°C. This is clear in Figure 5 where the average Ms temperature of all the samples prepared is reported as a function of the gold content.

NiTiAu

The two alloys of NiTiAu show a transformation peak in the as cast state. Furthermore this can be greatly changed according to the thermal treatment. This is particularly evident in the case of $Ni_{36.2}Ti_{50}Au_{13.8}$ alloy that we will present here in more detail. Figure 6 is a comparison of the calorimetric analysis performed in the as cast state (A), on a sample which was annealed at 750°C for one hour and on another sample which has been hot worked at 800°C. In the as cast state it is present a very broad peak with two smaller signals superposed at about 50 and 60°C. On heating it is evident that the peak is a composed one. Performing a thermal treatment at 750°C the large peak is greatly reduced in intensity whilst the two smaller peaks are still present (Figure 6-B). The transformation enthalpy is drastically reduced from 4.92J/g to an average value of 1.1J/g. On the other hand if the material is processed by hot working at a temperature of 800°C (Figure 6-C) the large transformation peak is restored with a smaller spread of the transformation temperatures and enthalpy values of 6J/g are restored. This effect can be obtained independently from performing the hot rolling procedure. Even only the thermal treatment at a temperature of 800°C led to enhancement of the calorimetric signal.

To investigate in greater detail the effect of this thermal treatment metallographic observation were done. Figure 7 compares the microstructure observed with a magnification of 200x in the as cast sample (a), in the sample annealed at 750°C (b) and in the sample annealed and hot worked at 800°C (c). It is clearly present a two phase structure which can be only hardly distinguished in the as cast alloy (the small clearer stripes), occupies more than 50% of the effective area in the sample annealed at 750°C and eventually is more regularly distributed in the sample annealed at 800°C.

From the samples which has been hot worked to a final thickness of 0.5mm a sample was taken (0.5 x 5 x 45mm^3) and used to characterize the shape recovery and pseudoelastic properties of the alloy. In Figure 8 are present two photograms taken from a video in which the shape recovery after a deformation of 8% is demonstrated. Recovery is obtained by fluxing hot heat with a dryer on the sample which is mounted in the bottom part of the deforming mandrel. The wire leaving the sample on the left is a K-type thermocouple used to monitor sample temperature. Of course in this configuration temperature precision is very low so that the number reported in the thermocouples reader on the right should be considered only for reference.

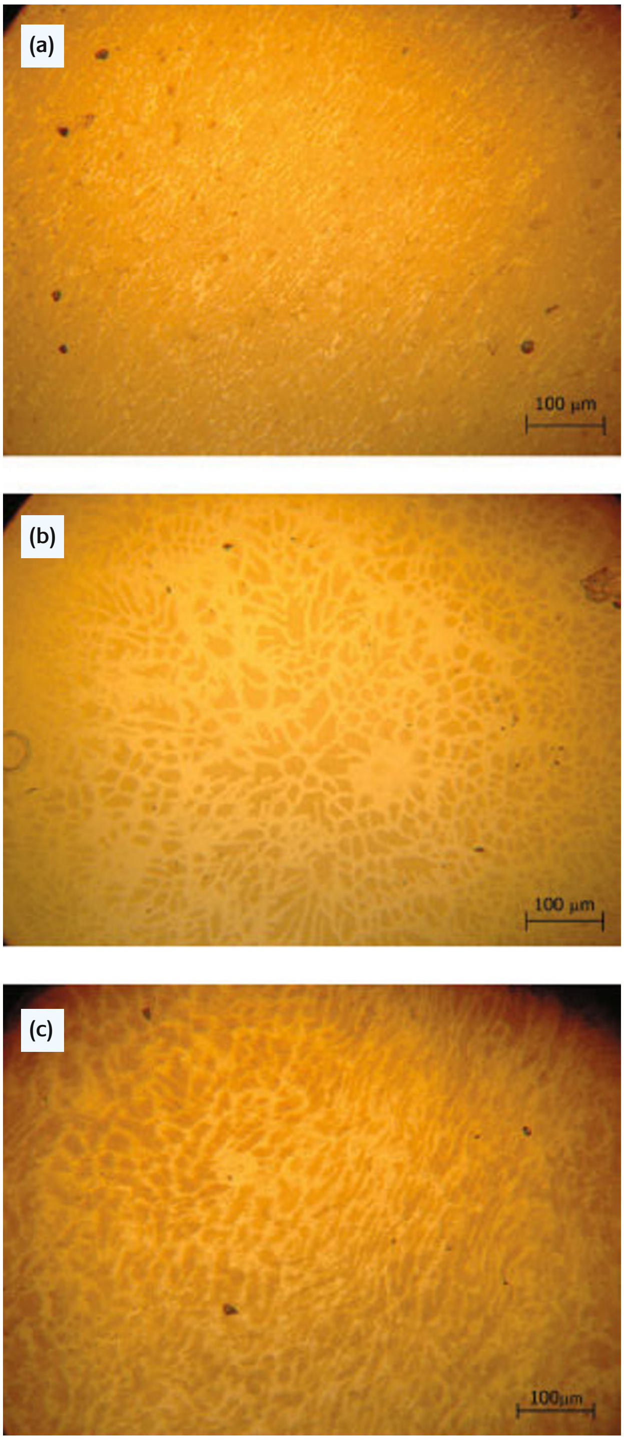

Figure 7

(a) microstrucutre of the $Ni_{36.2}Ti_{50}Au_{13.8}$ *alloy chemically etched. Observations were made at room temperature hence in martensitic phase (b) similar image for the sample annealed at 750°C. (c) similar image for the sample annealed at 800°C*

Discussion

The calorimetric characterization performed on the AuCuZn demonstrated the great sensitivity of this alloy to stoichiometry concerning the transformation temperature. This, together with the very high Zn content pose serious problems to its metallurgy process. It has been demonstrated the hot workability of the alloys if they are maintained in a protect environment but cold workability still is a problem. At present it was not possible to perform a reliable shape recovery test.

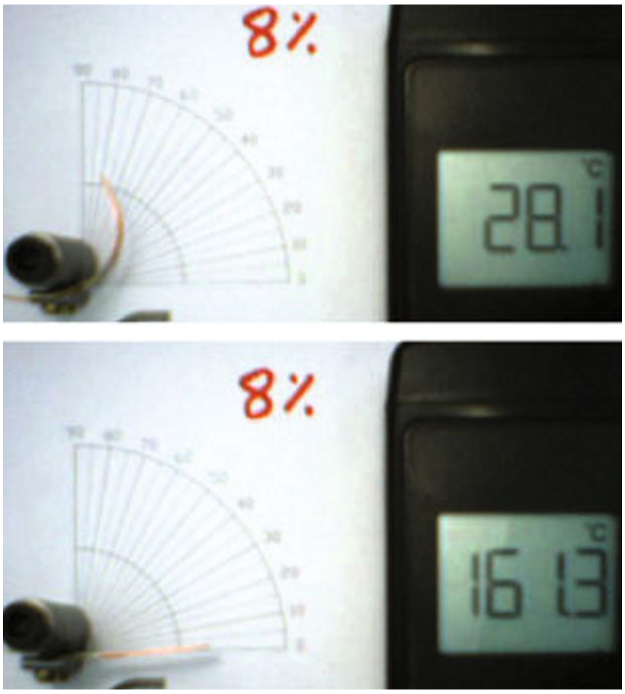

Figure 8

Demonstration of the shape recovery for a sample of $Ni_{36.2}Ti_{50}Au_{13.8}$ *deformed at room temperature with a maximum deformation of 8%*

Turning to NiTiAu system it demonstrated really a strong potential. Production route and identification of processing procedure still will require a lot of work. In this case what should be understood in greater detail is the role of Ni in changing the transformation temperatures when comparing to the binary AuTi. This alloy has high transformation temperature. Ni addition dramatically decreases them. At the same time the NiTi equiatomic alloy can withstand for such a strong substitution of Ni with Au still preserving exceptional transformation properties. The results obtained with the annealing procedure indicate that Ni segregation in the matrix could play a major role. If anneal is performed at a too low temperature a two phase structure is formed with an excess of Ni present in the secondary phase. It seems that this phase is detrimental for the transformation as proved by calorimetric analysis (Figure 6B). On the other hand if the thermal treatment is performed at temperature close to the maximum of the solubility gap of the AuNi system the initial properties are restored. What is not still clear is the role of this secondary phases on alloy workability. Preliminary test seems to suggest that the more homogeneous structure is beneficial for deformability too.

Eventually a short comment should be done on the images presented to demonstrate 8% shape recovery. What is presented here is only the initial and final position reached by the sample at the beginning and at the end of the heating step. Previously the sample was completely bent over the deforming mandrel. The starting position is reached because of the elastic springback. Even if not reported here for space reasons it has been verified that the springback is dramatically reduced if the material is bent over the mandrel at high temperature in the austenitic phase and cooled in this position. Incidentally this demonstrates also the pseudoelastic property of the sample as it can withstand a shape deformation as high as 8% in the austenitic phase and perfect recovery in isothermal conditions. No quantitative evaluation can be derived by this test but they qualitatively demonstrate the very good shape memory property of this alloy.

Conclusions

It has been reported here on results obtained in the calorimetric, microstructural and functional characterization of gold alloys which have a thermoelastic martensitic transformation and for this reason are good candidates for exhibiting shape memory and/or pseudoelastic properties.

1 AuCuZn is a good candidate for spanning large transformation temperature ranges with a small stoichiometric modification, its hot workability is very good, major problems arise when cold workability is considered;
2 It has been developed a technique to control the melting procedure in order to guarantee the final Zn content of the alloy, to ensure great homogeneity and avoid excessive grain growth;
3 It has been demonstrated the possibility to substitute Ni in the binary NiTi alloy up to 27at% of Au still preserving the martensitic transformation;
4 Especially the alloy with around 14at% of Au demonstrated exceptional recovery properties;
5 The fundamental role of the thermo-mechanical history on the transformation properties has been addressed and a competitive role of a Ni-rich phase segregating from the matrix suggested.

About the authors

Dr. Stefano Besseghini received his Scientific High School Certificate of Education, from Liceo Scientifico Carlo Donegani Tirano (SO) in 1984/85. In the following years he read Physics obtaining his Laurea (Applied Physics: Atomic, Molecular and Solid State Physics) from Università degli Studi di Milano in 1991/92. He specialised in Science and Technology of Materials with a Degree from Università degli Studi di Milano in 1994/95. Since September 1996 he is working at IENI-CNR (Unità di Lecco), first as Research Fellow, then as Researcher. Since 2003 he is head of laboratory of the IENI branch in Lecco. His main work interests are Magnetic and NiTi-based Shape Memory Alloys (SMA), both as theoretical research subjects and in industrial and biomedical actuation applications. He also works on the synthesis and characterisation of precious alloys. He takes part, also with management tasks, in several collaboration and technology transfer projects with Italian companies and abroad.

Dr. Francesca Passaretti graduated in Industrial Chemistry. She is since 2001 researcher (faculty) in the Italian National Research Council (CNR) based in Istituto per la Energetica e le Interfasi (IENI), Lecco. Her research interests cover metallurgy in general, precious metallic alloys for jewelry, shape memory alloys and microscopy. She has educational responsibilities as contracted Professor at Università di Milano Bicocca where she teaches physics of metallic alloys in the “Jewelry Science and Technology” curriculum of the Material Science Faculty.

Dr Paolo Fabbro received his Scientific High School Certificate of Education in 1972 in Arezzo. Then he graduated in Chemistry in 1979 in Florence. Since 1980 he is working at UNOAERRE, a world leader company for jewellery production. In UNOAERRE Group he is Director of the Research & Development Dept., Director of the Foundry, Findings and Components Division and Director of Chemical and Metallurgical Labs. He is a member of AIM; he masters more than 800 special alloys in his job along with a notable technical know-how of production machines at any level of the production cycle, from foundry to polishing. He also acquired a remarkable know-how, through specific courses and stages, in the subject of work safety. He joined, also as speaker, many conferences relating the most recent world discussions on metallurgy of precious and not-precious metals.

Dr Franca Ricciardi received her Classical School Certificate of Education in 1981 at Arezzo. Then she graduated in Languages in 1985 and got the Certification for Translator and Interpreter. Then she frequented The IULM University in Milan for specialization. Since 1990 she is working at UNOAERRE, a world leader company for jewellery production. In UNOAERRE Group she was at the beginning technical translator, then she ran the General Secretary. In 1999 she became Assistant Product Manager of the Findings and Components Division. In 2001 she became Product Manager and Marketing Manager of the Findings and Components Division. Since 2005 she is Product Manager UNOAERRE and Development Product Coordinator of finished products. Moreover she joins the Dept. of Research & Development with the task of implementing the results of this dept. into production. She acquired in the years a notable know-how both in the field of marketing from the individuation of mega trends up to the launching of products in the market, and in the field of technical managing of statistics, reports, budget as well as technicalities of production in general.

Dr. Elena Villa graduated in Physics, Università degli Studi di Milano, in 1993/94. She specialised in Science and Technology of Polymers in 1996/1997.
She is since 2001 researcher (faculty) in the Italian National Research Council (CNR) based in Istituto per la Energetica e le Interfasi (IENI), Lecco. Her field of activity is the microstructural characterization of innovative alloys by thermal and mechanical analysis (DSC, TG/DTA, DMTA and mechanical tests). She is involved also in the collaboration with different kind of industries to develop new industrial applications of Shape Memory Alloys.

Acknowledgements

Thanks are strongly due to Mr. Giordano Carcano and Mr. Marco Pini for the fundamental technical support given in the development of present work.

References

1 K Otsuka., X Ren., *Progress in Material Science*, 2005, **50**, 511-678
2 G.B. Brook, *Gold Bull.*, 1973, **6**(1)
3 G.B. Brook, R.F. Iles, Gold Bull., 1975, 8(1)
4 O.I. Velikokhatnyj, I.I. Naumov, & V.Z. Bashirov, (1992). *Fizika Metallov i Metallovedenie*, (12), 30-40
5 A. Nagasawa, T. Makita, N. Nakanishi, M. Iizumi, & Y. Morii, (1986). Alloys. *Metallurgical transactions. A, Physical metallurgy and materials science*, 19 A(4), 793-796
6 H. Terauchi, S. Iida, K. Tanabe, K. Kikukawa, H. Maeda, & M. Hida, et al. (1983). *Journal of the Physical Society of Japan*, **52**(12), 4041-4043
7 M. Mori, Y. Yamada, & G. Shirane, (1975). Soft Phonon Mode At The Martensitic Phase Transformation Of Aucuzn//2. *Solid State Communications*, **17**(2), 127-130
8 H. Seol, T. Shiraishi, Y. Tanaka, E. Miura, Y. Takuma, & K. Hisatsune, (2002). *Journal of Alloys and Compounds*, **339**(1-2), 144-148
9 M. Ahlers, (1980). Influence Of Do//3 Order On The Martensitic Transformation In Cuznau And Cuznal Alloys. *Zeitschrift fuer Metallkunde/ Materials Research and Advanced Techniques*, **71**(11), 704-707
10 T. Suzuki, T. Yoshida, T. Miyasaka, *J. Nippon Dent. Univ.* **73** (4),(1985) 883
11 M Cortie, Wolff, F Levey, S Taylor, R Watt, R Pretorius, et al. *Gold Technol* 1994;14:30
12 F.C. Levey, M.B Cortie, L.A. Cornish *Metall Mater Trans A* 2000;31 A:1917
13 F.C. Levey, M.B. Cortie *Mat Sci Eng A-Struct* 2001; A303:1
14 M.B. Cortie, FC Levey. *Intermetallics* 2000;8:793
15 S. Urbano, A. Manca, S. Besseghini, G. Airoldi, *Scripta Materialia*, **52**(4), 2005, pp 317-321
16 H.C. Donkersloot, Jhn. Van Vucht, *J. Less. Common Metals*, **20**(2), pp. 83-91
17 S.K. Wu, C.M. Wayman, (1987) *Metallography*, **20** (3), pp. 359-376
18 S.K. Wu, C.M. Wayman, (1987) *Scripta Metallurgica*, **21** (1), pp. 83-88