C.A. Imamalizade

Manufacturing of nitinol-based alloys by using modern technology: A short review

Azerbaijan State Oil and Industry University, Baku, Azerbaijan, cimamelizade@gmail.com

The paper provides a brief review of literature data on the synthesis, processing, structure, mechanical properties, and application of nitinol and alloys based on it, which are promising functional materials found application in a number of high technologies. In addition, machine learning methods were applied to predict the temperatures of phase transformations.

Keywords: shape memory alloys, nitinol, and alloys based on it, machine learning, microstructure, thermomechanical behavior.

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The purpose of the article is to discuss the methods of synthesis and thermomechanical processing, structural features, as well as the use of alloys based on nitinol in modern high technologies.

A very extensive literature review of works in the field of research of materials with a memory effect does not allow us to consider them all in detail. Therefore, the following is only a brief part of all available literature in this area.

Modern scientific progress is unthinkable without the search and creation of new materials with functional properties. Such promising materials include shape-memory alloys. This contributed to the extensive popularity of this material for a wide range of applications [1-5].

Shape memory alloys (SMAs) are such kinds of alloys whose technical properties contribute to solve complicated challenges in the modern world. SMAs have 2 main technical properties used in modern industry: shape memory effect and superelasticity. The shape memory effect helps SMAs to recover their initial shape during the thermomechanical cycle. Superelasticity helps SMAs to resist extra-large loads without plastic deformation during only mechanical cycles [1-3].

SMAs are used in a wide variety of applications in modern industries. They are used as dental wires, in joining broken bones using metal plates, and in the construction of sensitive medical devices in bioengineering applications [4]. They are also used as tubes and wires in applications with hot fluids. SMAs are ideal as they can return to their original shape even in a heated environment [1,2].

SMAs are applied also in civil engineering, for instance, in bridge construction. SMAs reduce vibrations, hence damping the natural frequency of different structures. This vibration-damping property has also been used in jet engines and launch vehicles [4]. One potential application for SMAs with high working temperatures is decreasing airplane noise [5].

Fig. 1 shows the application of SMAs in medical and jet engines aerospace engineering.

Nitinol (NiTi) is one of the most famous alloy among the SMAs family and consist of a nearly equal amount of nickel and titanium. Despite the fact that the region of homogeneity of this alloy is 50-56 at% Ni, from a technical point of view, alloys from the region of 50-52 at% Ni are the most applicable (Fig. 2) [6].

Therefore, in the literature, there are a number of works devoted to the study of alloys from this range of compositions [6-12]. Usually, to improve the thermomechanical properties, these alloys are alloyed with a third element: hafnium, zirconium, and silicon [13-17]. More complex compositions are also used [18, 19].
The rapid development of new technologies imposes the most important and diverse requirements on materials. However, traditional methods for discovering new materials, such as empirical trial and error and density functional theory (DFT), usually require a long research time. Machine learning (ML) can significantly reduce computational costs and reduce research time, i.e., it is one of the most efficient ways to replace DFT calculations and repetitive lab experiments. Machine learning is used to discover new materials, predict material and molecular properties, study quantum chemistry, and design drugs [20-23].

A number of investigations are devoted to various methods of manufacturing and heat treatments from features were investigated in NiTiHf and NiTiFeCuPd alloys by using various ML methods. In [22] Gauss Process Regression was used to predict transition temperatures of nitinol-based alloys. Authors of [23] used the artificial neural network to find the best parameters for manufacturing NiTi-based alloys. It was found that cutting parameters, such as feed rate, cutting speed, and depth of cut, have a significant influence on the machining process of this alloy. Deep Learning was applied to predict the conventional yield strength, conventional tensile strength, and unit elongation of NiTi-based alloys [24]. It was obtained that, Deep Learning showed higher performance compared with Random Forest which also was used in this article.

The study [25] presents the optimization of cutting parameters, such as feed rate, cutting speed, and depth of cut, to obtain appropriate and acceptable values for critical outputs, such as cutting forces, tool wear, surface roughness, and dimensional deviation of machined parts. This study showed that the developed empirical model can predict the main results of turning operations with high accuracy. Cutting speed has been shown to play a critical role in controlling output data such as tool wear, surface roughness, and cutting forces (Fig. 3). With a lower cutting speed, relatively higher feed, and depth of cut, material removal rate can be maximized when machining NiTiHf HTSMA.

The optimization of parameters of electrochemical machining was investigated by using a deep neural network, Taguchi regression, and response surface method. The results obtained by the authors were compared among each other and discussed in the work [7].

In the literature, there is a huge number of works devoted to various methods of manufacturing and heat treatments [27-35], the study of the influence of chemical composition on phase formation and transformation [35-41], crystal structure [41-46], thermomechanical properties [45-48], improving and optimization of manufacturing parameters [30, 49-53]. Let’s briefly discuss some of these works.

The machinability of Ti-rich Ni_{32.5}Ti_{32.5}Hf_{35} and Ni-rich Ni_{30.5}Ti_{29.2}Hf_{20} high-temperature shape memory alloy (HTSMA) wires were investigated in the 750-825°C temperature range [8]. Tensile testing and differential scanning calorimetry have been used to determine the thermomechanical behavior of hot-rolling alloy solutionized and then aged NiTiHf wires. It was obtained that, the ideal temperature of rolling for Ni-rich NiTiHf wires is over H-phase dissolution temperature (about 800°C). The reason for such a temperature is to prevent the wire from getting more brittle because of the H-phase effect and restrict compositional instability at the surface of the wire caused by HfO₂. The properties of oxide layers created during the rolling process and then heat treatments have been compared to solve several problems related to NiTiHf wire processing.

A new combinatorial alloy synthesis method (suspended droplet alloying - SDA) has been proposed for effective alloy discovery [26]. In this method, a laser is used to melt alloyed or elemental wires fed at a controlled rate to get a specific chemistry. The synthesized sample...
was subjected to heat treatment for various periods of time. The microstructural and chemical inhomogeneity was assessed using quantitative electron microscopy and X-ray diffraction. In addition, the phase transition temperatures of the samples were compared to cast and heat-treated (reference) samples (Fig. 4). As a rule, long-term annealed samples showed a limited local deviation from the target chemical composition (±1 wt.%) while showing an expected phase distribution with the fairly homogeneous microstructure. According to this work, the original sample has a lower temperature of transformations due to chemical inhomogeneity, while the heat-treated samples have a similar transformation temperature to the reference sample.

![Fig. 3. Experimental and predicted values depending on cutting speed (constant f = 0.12 mm/rev, ap = 0.8 mm) (a) and feed rate (constant V = 70 m/min, ap = 0.8 mm) (b) [25].](image)

NiTi-20Hf HTSMA with the composition of 50-51%Ni has been manufactured and tested by using thermal cycling, heat treatments, and hardness testing [49]. For all conditions, transformation temperatures have been measured, and has been observed negative correlation between transformation temperature and Ni content up to 50.5%. However, above 50.5% Ni content, transformation temperature has increased or has been stable depending on the homogenized condition or age. Similar behavior has been observed in hardness test results. Above 50.5% Ni contents, NiTi-20Hf alloys have illustrated higher hardness results in 550°C for 3 h aging conditions.

Laser powder bed fusion was extensively investigated in the shape memory alloys field, primarily NiTi alloys to adapt microstructures and create complex geometries [30]. However, according to the authors, the processing of HTSMA still remains unknown. This paper investigated the dependence of the functionality of this alloy on the effect of process parameters (PP). Microstructure and the shape memory properties of additively fabricated high-temperature NiTiHf alloys were characterized over a large range of PP (hatch spacing, scan speed, and laser power) and correlation with energy density was found. The results will help for optimizing fabrication parameters in future works related to HTSMA.

Authors of [34], for the first time, laser welding has been used to increase the strength of Ni-rich NiTiHf HTSMA. Initial material aged at 500 °C for 3 h, then air cooled. After these heat treatments, defectless joints with conductive weld conditions were obtained. Microstructural properties, facilitated by using synchrotron X-ray diffraction and microscopy, showed that at room temperature, the melting zone consists of a single-phase martensitic structure. However, in base material melting zone consists of martensite and H-phase precipitates. Loading at constant temperatures (30 °C for martensite, 200 °C for austenite) both of phases showed equal strength and nearly perfect superelasticity.

In [41], the microstructure and mechanical properties of rapidly solidified Ti_{50-y}Ni_{50+y}Hf_{x} (x = 0, 2, 4, 6, 8, 10, and 12 at.%) and Ti_{50-y}Ni_{50+y}Si_{x} (y = 1, 2, 3, 5, 7, and 10 at.%) shape memory alloys (SMAs) were investigated. The sequence of the phase formation and transformations in dependence on the chemical composition is established.

Rapidly solidified Ti-Ni-Hf or Ti-Ni-Si SMAs are found to show relatively high yield strength and large ductility for specific Hf or Si concentrations, which is due to the gradual disappearance of the phase transformation from austenite to twinned martensite and the predominance of the phase transformation from twinned martensite to detwinned martensite during deformation as well as to the refinement of dendrites and the precipitation of brittle intermetallic compounds. The authors show a formation of continuous series of solid solutions exists between the
HfNi and NiTi phases at the high temperatures (> 1448 K) (Fig. 5).

Scanning electron microscopy, transmission electron, and X-ray diffraction (XRD) were used to investigate how the amount of zirconium (0-20%) affects to morphological features of martensitic transformation and phase composition of ternary Ni-Ti-Zr alloys [44]. In a large range of temperatures, the electrical resistivity of ternary Ni-Ti-Zr alloys was measured and critical temperatures were calculated. In addition, based on XRD data the complete diagram of martensitic transformations B2 ↔ B19 of ternary Ni-Ti-Zr HTSMA which occurs in a range between 32-50 K has been constructed. It was shown that the increasing amount of Zr in alloys results in increasing martensitic transformation temperature.

**Conclusion**

In this article, a number of works on nitinol-based alloys, their synthesis, heat treatment, crystal structure, and thermomechanical properties are considered and analyzed. However, the presence of a large number of unexplored problems requires further research in these areas.

Chingiz Abbas Imamalizade – doctoral student, Azerbaijan State Oil and Industry University.

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Ч.А. Імамалізаде

Виробництво сплавів на основі нітинолу на основі сучасних технологій: короткий огляд

Азербайджанський державний університет науки та промисловості, Баку, Азербайджан, cimamelizade@gmail.com

У статті подано короткий огляд літературних даних щодо синтезу, переробки, структури, механічних властивостей і практичного застосування нітинолу та сплавів на його основі, які є перспективними функціональними матеріалами та знайшли застосування в ряді високих технологій. Для прогнозування температур фазових перетворень застосовано метод машинного навчання.

Ключові слова: сплави з пам'ятю форми, нітинол та сплави на його основі, машинне навчання, мікроструктура, термомеханічна поведінка.