National R&D Institute for Nonferrous and Rare Metals

NEW MATERIALS AND TECHNOLOGIES LABORATORY

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NEW HIGH ENTROPY ALLOYS WITH SUPERIOR CHARACTERISTICS FOR MEDICAL APPLICATIONS

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ABSTRACT

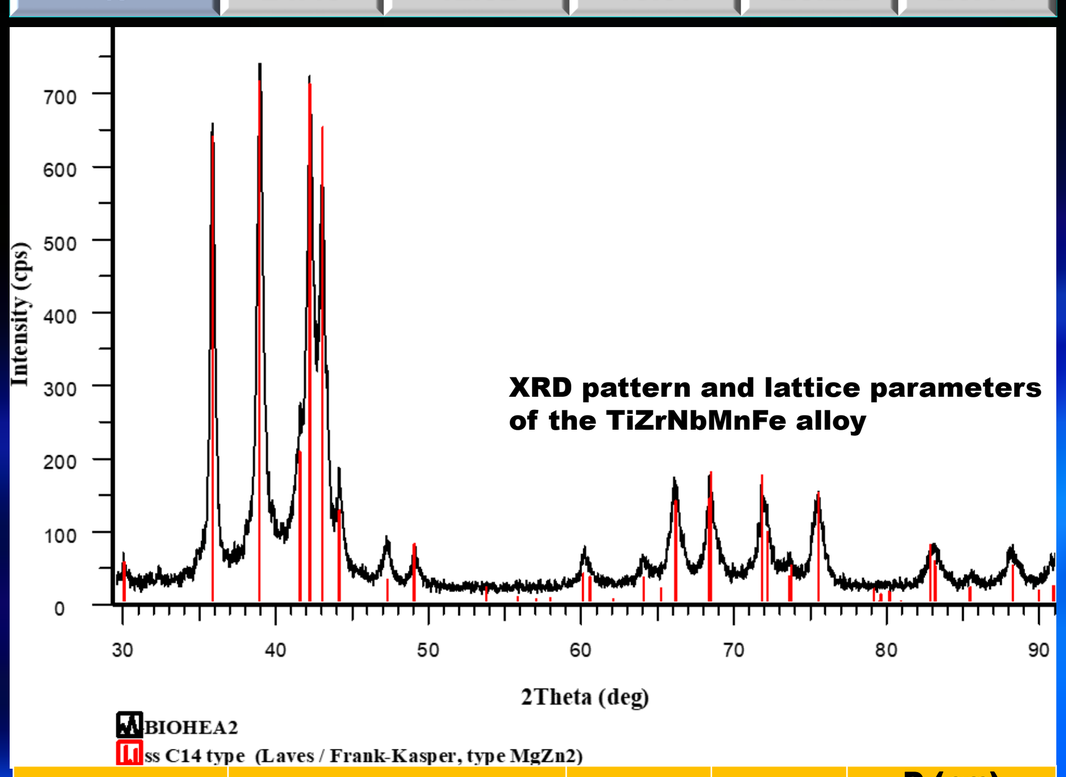
The paper investigates a new type of high entropy alloys (HEA) for biomedical applications. High entropy alloys represent a new alloy family that consist of five or more elements in equal or near equal percentage and which form complex solid solution structures. An alloy based on the TiZrNbFeMn system was obtained by induction melting/casting in vacuum and inert atmosphere. All the constituent metals exhibit a high degree of biocompatibility, with remarkable potential for biomedical applications. The influence of the processing parameters (melting temperature, vacuum, solidification rate, time) on the microstructure and mechanical/corrosion resistance properties of the new alloy was investigated. Optical microscopy and X-ray diffraction characterization results showed a singular solid solution phase with a high degree of grain refining. The investigated alloys exhibit high hardness, with low modulus of elasticity and moderate strength, which shows capability in avoiding stress shielding and prevent bone resorption in medical implants. The nature of the elements contained by the selected high entropy alloys and the predominant solid solution structure determined high corrosion resistance in physiological media, compared to the conventional alloys. The mechanical properties and corrosion resistance in simulated body fluids of the obtained alloy are higher than those of 316L stainless steel and Ti–6Al–4V.

EXPERIMENTAL

The preparation of the TiZrNbMnFe high entropy alloys was carried out in a Linn MFG – 30 induction furnace with vacuum/inert atmosphere. High purity elemental Ti, Zr, Nb, Mn and Fe were used as raw materials. The alloys were re-melted several times to ensure a uniform composition. The chemical composition of the alloy was determined by optical emission spectrometry in inductively coupled plasma (ICP-OES) using an Agilent 725 spectrometer. Optical microscopy investigations were performed with a Zeiss Axio Scope A1m Imager microscope. The phase structure was analyses by X-ray diffractometry (XRD) with a BRUKER D8 ADVANCE diffractometer. The Vickers microhardness of the samples was measured at room temperature using an Anton Paar MHT10 module with an applied load of 2N and a slope of 0.6 N/s.

CHARACTERIZATIONS AND RESULTS

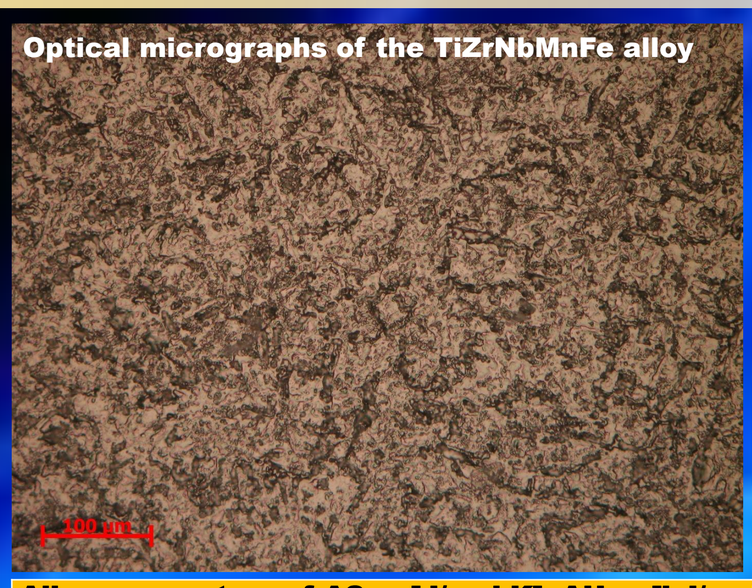
Chemical composition, at .%					
Element	Ti	Zr	Nb	Mn	Fe
%	24.45	12.32	13.87	23.22	26.14

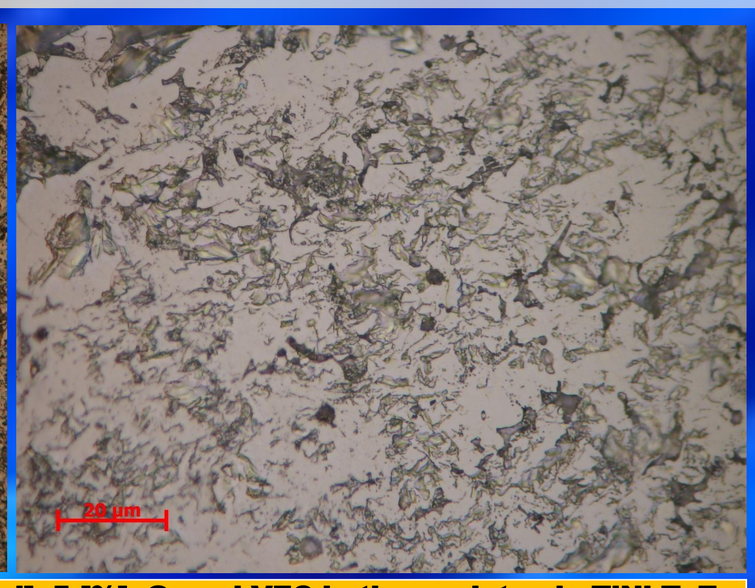


XRD pattern and lattice parameters of the TiZrNbMnFe alloy

Phase	Space group	a (Å)	c (Å)	D (nm) Scherrer
ss C14 type	Hex. P63/mmc (194)	5.032	8.221	13

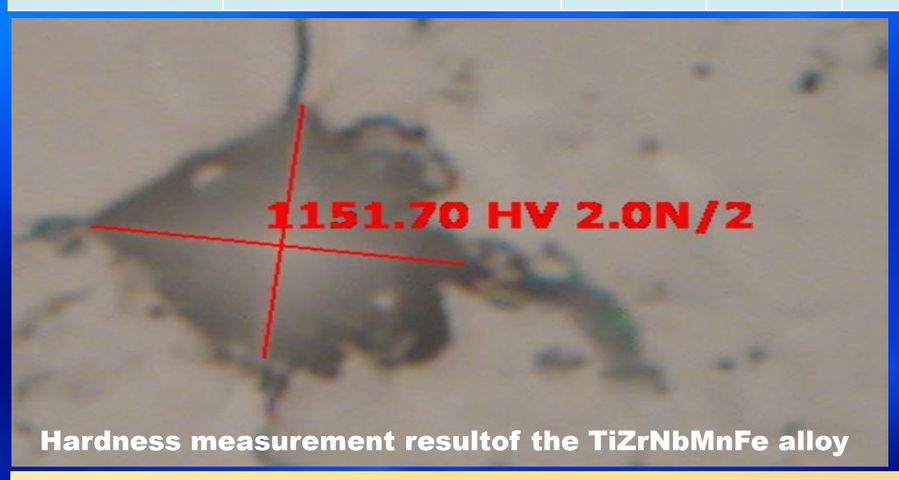
Optical micrographs of the TiZrNbMnFe alloy





Alloy parameters of ΔS_{mix} [J/mol K], ΔH_{mix} [kJ/mol], δ [%], Ω, and VEC in the equiatomic TiNbTaZr and TiNbTaZrX (X = Cr, V, Mo, W, Fe) alloys.
*Todai et al (2017)

Alloy	Δs_{mix}	Δ_{Hmix}	δ	Ω	VEC
TiZrNbTa*	1.42R	2.5	5.3	11.6	4.50
TiZrNbTaFe*	1.61R	−10.1	8.4	3.2	5.20
TiZrNbMnFe	1.61R	-13.25	7.87	1.88	5.87
TiZrNbTaMo*	1.61R	−1.8	5.9	19.7	4.80
TiZrNbTaW*	1.61R	−3.2	5.8	11.5	4.80
TiZrNbTaV*	1.61R	0.3	6.7	101	4.60
TiZrNbTaCr*	1.61R	−3.7	8.2	8.9	4.80
TiZrNbTaHf*	1.61R	2.7	5.5	12.4	4.40



Hardness measurement resultof the TiZrNbMnFe alloy

Mechanical properties and corrosion resistance of biocompatible metallic materials

Material	Young's modulus, [GPa]	Yield strength, [MP]	Ultimate tensile strength, [Mpa]	Corrosion rate in simulated body fluid, [mm/year]
Stainless steel 316L	190	500	750	0.0031
Ti–6Al–4V	110	800	900	0.0016
Cobalt-Chrome	230	1000	1200	0.0034
TiZrNbTa	48	700	880	~ 0.001
Human bone (limb)	30	121	130	-

CONCLUSIONS

The experimental works demonstrated the remarkable potential of the high-entropy alloys based on the TiZrNbFeX system (X = Ta, Mn, Mo) for application as biomedical materials. X-ray diffractometry and optical microscopy analyses revealed a single-phase structure for the TiZrNbMnFe HE alloy, with a fine-grained dendritic morphology. The alloy exhibited high hardness, with a maximum value for the determined hardness of approximately 1152 HV. The mechanical tests lead to very low values of the Young's modulus for the TiZrNbTa alloy, with a minimum result of 48 Gpa, which is very close to the elastic modulus of human bone. Also, the corrosion rate of the alloy in simulated body fluids (SBFs) was of approximately 0.001 mm/year. The mechanical properties and corrosion behavior in simulated body fluids of the studied alloys are better than those of 316L stainless steel and Ti–6Al–4V alloy used presently.

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