Designing high-entropy brazing alloys for joining titanium and refractory metals

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Standard titanium filler metals for vacuum brazing do not satisfy strength and temperature requirements for new applications such as electro-chemical power sources, reactors, or spacecraft devices. Uncontrolled, multiphase microstructures formed in brazed joints made by these filler metal limit optimization of their mechanical properties or corrosion resistance.

This paper discusses a design approach to formulate new titanium brazing alloys that may obtain a uniform single- or two-phase microstructure, preferably with solid solutions as the main phase. The design approach is based on increasing a mixing entropy of the alloy composition and application of the Hume-Rothery rules to select combination of metals in the alloy composition.

Three alloys were designed and manufactured in the form of amorphous foils or powders:

- Brazing alloy TiBraze620 containing Zr-(10-12)Ti-(19-21)Ni-(6-8)Nb-(1-2)Hf wt.%,
- Brazing alloy TiBraze625 containing Zr-(10-12)Ti-(19-21)Ni-(7-10)Mo-(1-2)Hf wt.%,
- Brazing alloy TiBraze920 containing Ti-(17-19)Zr-(19-21)Ni-(19-21)Cu-(10-12)Nb wt.%,

Some designed and tested alloys are represented in Table 1. Properties of metallic components included in designed alloys are listed in Table 2. Brazing alloys TiBraze620 and 625 are manufactured in the form of amorphous foils 60-70 microns thick, 70-75 mm wide. The alloy TiBraze920 is the prealloyed spherical powder having particle size -170 mesh (-88 microns) or -140 mesh (-106 microns).

Table 1

Compositions of prealloyed brazing alloys

Brazing alloy	Compositions		Brazing temperature, °C
	wt.%	at.%	
TiBraze620	61.7Zr-10.4Ti-19.5Ni-7Nb-1.3Hf	51.7Zr-16.7Ti-25.4Ni-5.7Nb-0.6Hf	830-850
TiBraze625	60.3Zr-10Ti-19.2Ni-9.4Mo-1.1Hf	50.8Zr-16.1Ti-25.1Ni-7.5Mo-0.5Hf	830-850
TiBraze920	31.3Ti-17.7Zr-19.6Cu-20.2Ni-11.2Nb	40.3Ti-12Zr-19Cu-21.2Ni-7.4Nb	900-940

When designing the brazing alloys, the following Hume-Rothery rules (H-R rules) were used:

1. Atomic radiuses of solute and solvent atoms must differ by no more than 15%:

2. The crystal structure of solute and solvent must be similar.

3. The solute and solvent should have similar electronegativity.

Table 2

Physical properties of alloy components

Metal	Atomic radius, Ȧ	Crystal Lattice	Electro-negativity	Heat of fusion, kJ/mol
Ti	1.45	hcp	1.54	14.15
Zr	1.59	hcp	1.33	14.00
Hf	1.56	hcp	1.30	27.20
Re	1.37	hcp	1.90	60.43
Cu	1.28	fcc	1.90	13.26
Ni	1.25	fcc	1.91	17.48
Mo	1.36	bcc	2.16	37.48
Nb	1.43	bcc	1.60	30.00

As principal elements of the alloys, titanium and zirconium are compatible with Re and Hf according to H-R rules #1 and #2, while only rule #2 with Cu, Ni, and Mo. Four elements of the alloys Re, Cu, Ni, Mo are compatible according to the rules #1 and #3. Ti and Nb are also close by rules #1 and #3. Thus, all metallic components are in agreement with Hume-Rothery rules although in different combinations.

The next step of designing effective brazing filler metals is optimization of their configurational (mixing) entropy. Calculation of mixing entropy of alloys was done according to the universal gas constant times the opposite of the sum of the product of the molar fraction of the alloy component and the natural logarithm of that molar fraction (Ref. 3).

By definition, the mixing entropy $\boldsymbol{E_{mix}}$ of the 5-components alloys is in the range $1.39R < \boldsymbol{E_{mix}} < 1.61R$, where $R = 8.31\ J \cdot mol^{-1} K^{-1}$ is universal gas constant. Calculated values of mixing entropy presented in Table 3 confirm that brazing alloys TiBraze620 and 625 are not high entropy alloys, while the TiBraze920 has the high entropy composition. We suggest that addition of rhenium can improve their compositions because rhenium matches titanium by H-R rules #1 and #2, while Nb and Molybdenum match titanium only by the rule #1.

Table 3

Calculated mixing entropy of brazing alloys

Brazing alloy	Mixing entropy, ***nR***, $J \cdot mol^{-1} K^{-1}$	High entropy alloy or not
TiBraze620	1.18R	No
TiBraze625	1.20R	No
TiBraze920	1.46R	Yes

Application of the high entropy alloy TiBraze920 resulted in high strength of brazed joints of titanium Grade 5. Shear strength at room temperature reached 580.9 MPa, while the standard titanium brazing alloy exhibited only 516.1 MPa. The difference in strength between high entropy TiBraze920 and standard BTi-5 alloys is larger at 600°C. Titanium joints brazed by TiBraze902 reached 300.2 MPa, while brazed by BTi-5 exhibited only 102.8 MPa.

Despite the 4-principal components alloys TiBraze620 and 625 are not high entropy before the application, they accept the high entropy compositions and appropriate properties after diffusion exchange between the base and filler metals during brazing. For example, when we braze molybdenum, it diffuses into the braze alloy, which becomes 5-principal components high entropy composition.

We can call "in vitro" the alloys like TiBraze920 that have high entropy composition before an application. In contrary, the alloys which build the high entropy composition only during the application we can call "in situ" alloys. For example, nonhomogeneous structures that when heated will mix into a high entropy composition and then interact as a brazing filler metal with the base materials being joined.

References

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