“Fabricating INVAR-COPPER composite by SPS”

Current status of structural materials

2018.06.20

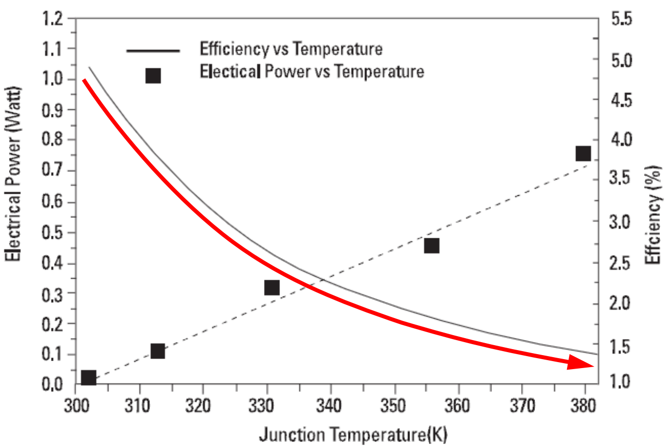
류종훈, 이준상, 윤국노

Introduction

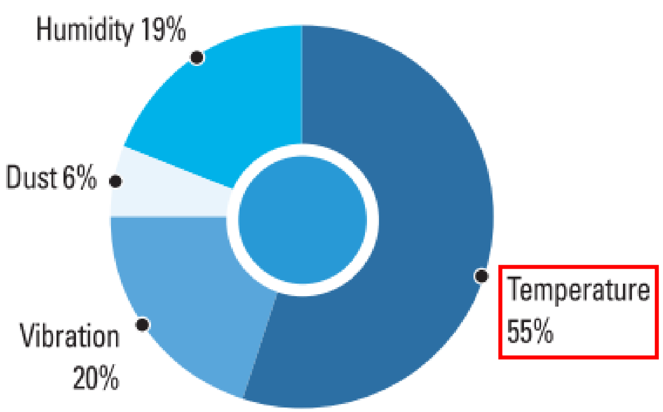
Needs of high-performance packaging for electronic devices

Application - Heat radiation materials

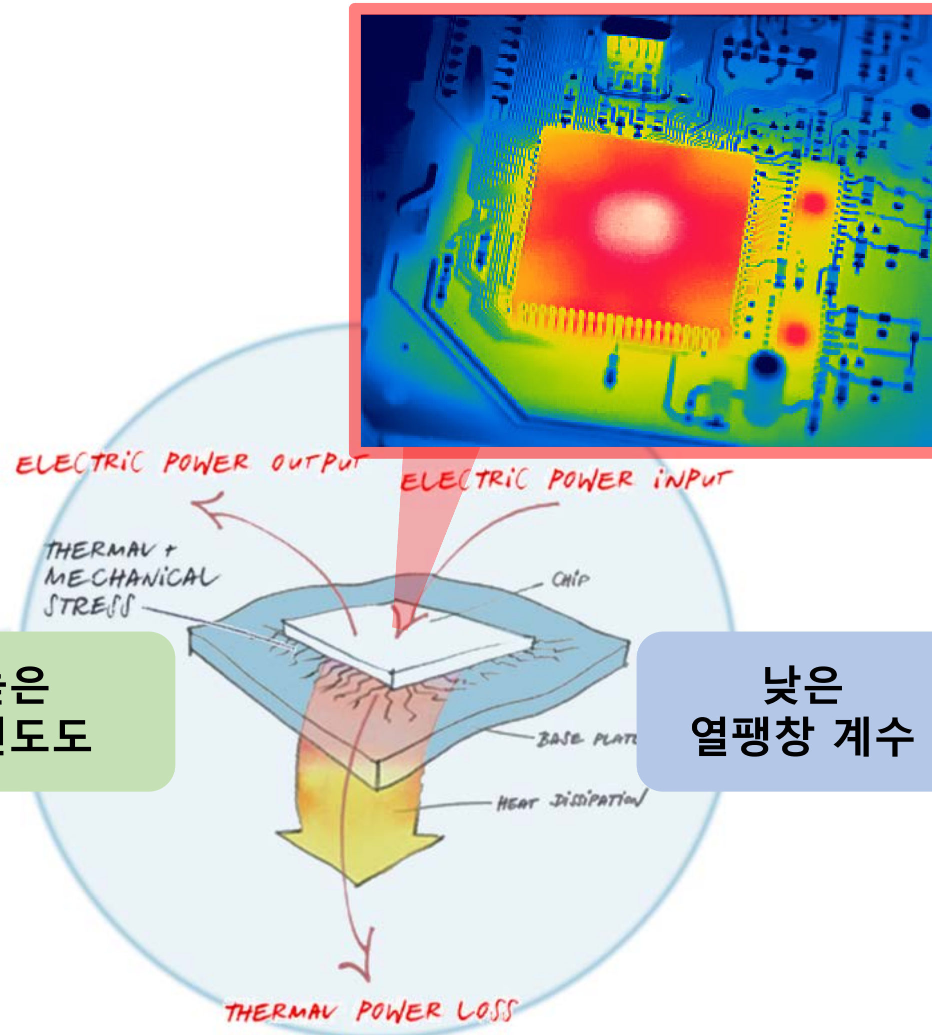
온도에 따른 전자 소자의 효율



대표적인 전자 소자의 불량의 원인



방열소재 및 방열접착 기술시장동향 및 사업화 이슈분석, 2015

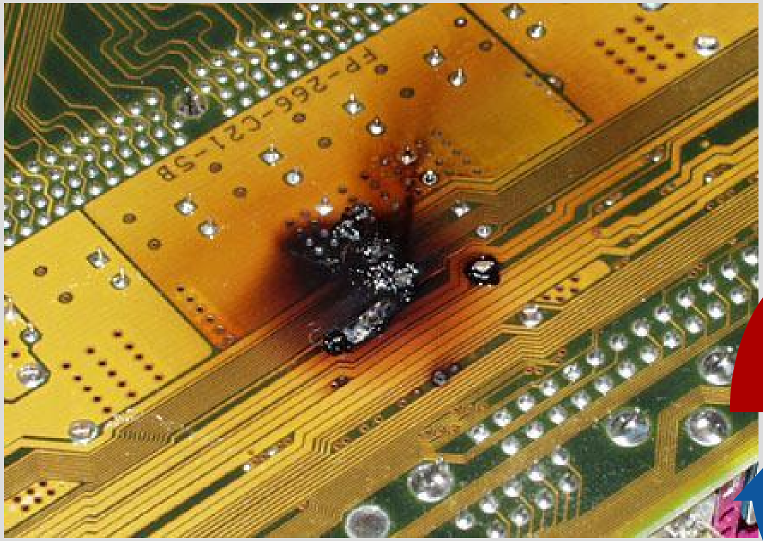


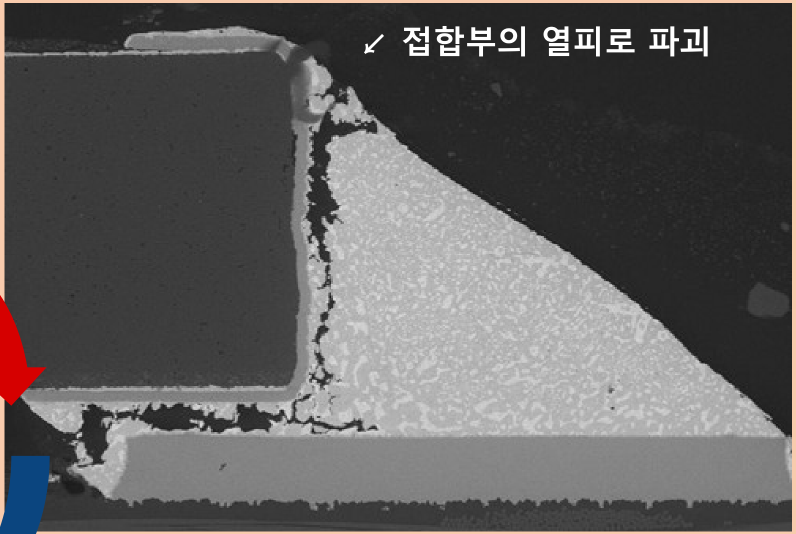
높은 열전도도

낮은 열팽창 계수

" 고성능 방열 소재의 개발이 요구됨 "

Needs of Heat radiation materials





세라믹 방열 재료

저열전도 / "저열팽창" 재료

→ 소자 과열로 효율 하락

금속 방열 재료

고열팽창 / "고열전도" 재료

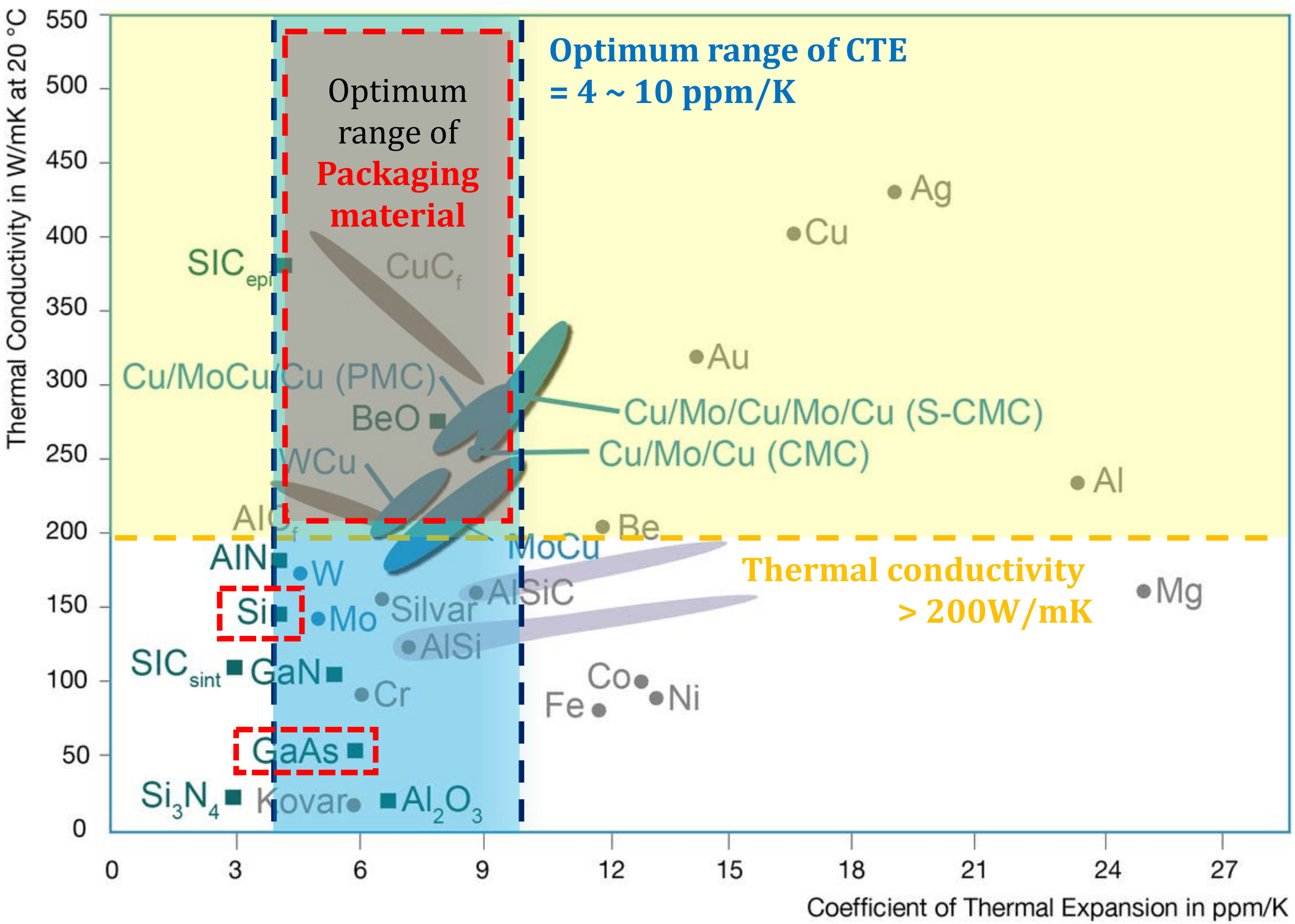
→ 열팽창 차이로 인한 파괴

서로 비례관계에 있는 열전도도 와 열팽창계수 간의 관계

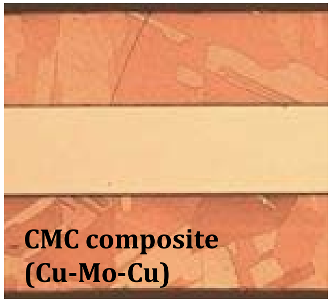
"고열전도도/저열팽창계수 재료의 개발의 어려움"

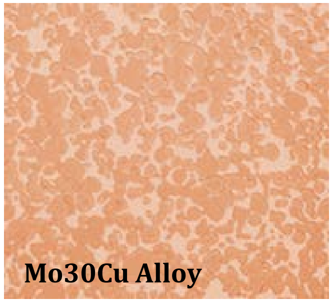
Optimum properties for heat radiation materials

1) Optimum condition



2) Economic problem





Mat.	Price ($/100g)
Cu	9.76
Fe	7.2
Ni	7.7
Mo	**45**

▶ **Substitution of Mo-Cu composite is need to be designed**

- which is cheap as well as having low CTE and high TC prosperities

Origin of INVAR effect

The Origin of the 'Invar' Effect

By R. J. WEISS†
Department of Mathematics, Imperial College, London

MS. received 1st *May* 1963

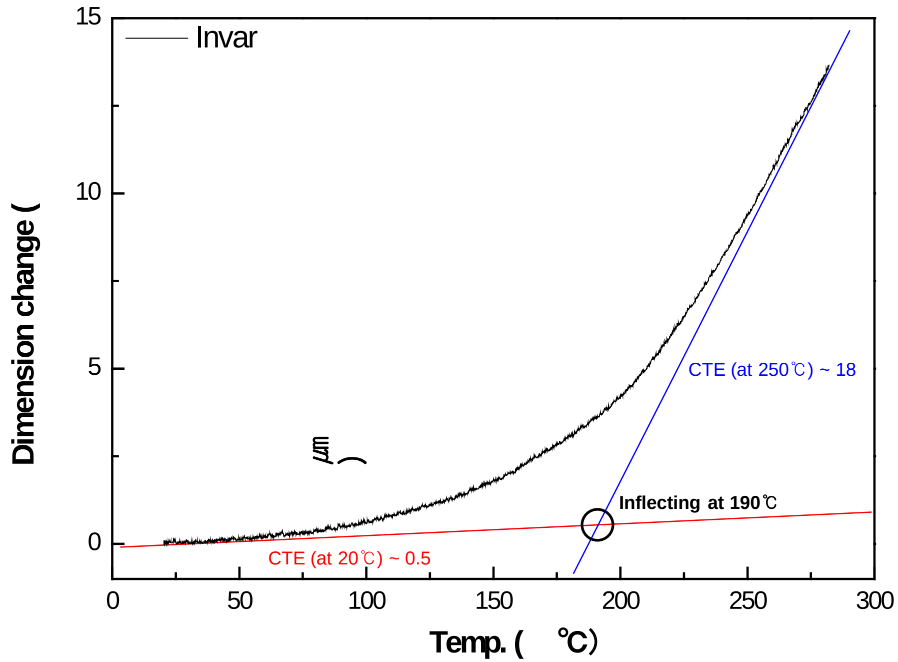
Abstract. The idea that there are two electronic configurations of iron atoms in a face-centred cubic lattice is extended to the iron–nickel alloy system. With a reasonable variation of the energy difference of these two configurations with nickel concentration it is shown that the 'invar' effect originates from the thermal excitation of the configuration with lower atomic volume in opposition to the normal anharmonic origin of expansion. The anomalous pressure dependence of the Curie temperature and the variation of Curie temperature with concentration for alloys containing 30–60% Ni are also shown to follow.

Table 1

The Approximate Values of Lattice Parameter, Spin per Atom, and Curie or Néel Temperature of the Two Electronic Structures of Gamma Iron obtained by Extrapolation from Alloy Data

	(1)	(2)	(3)	(4)	(5)
γ_1 (lower level)	f.c.c.	3·54	Antiferro-magnetic	∼0·5	∼80
γ_2 (upper level)	f.c.c.	3·64	Ferromagnetic	∼2·8	∼1800

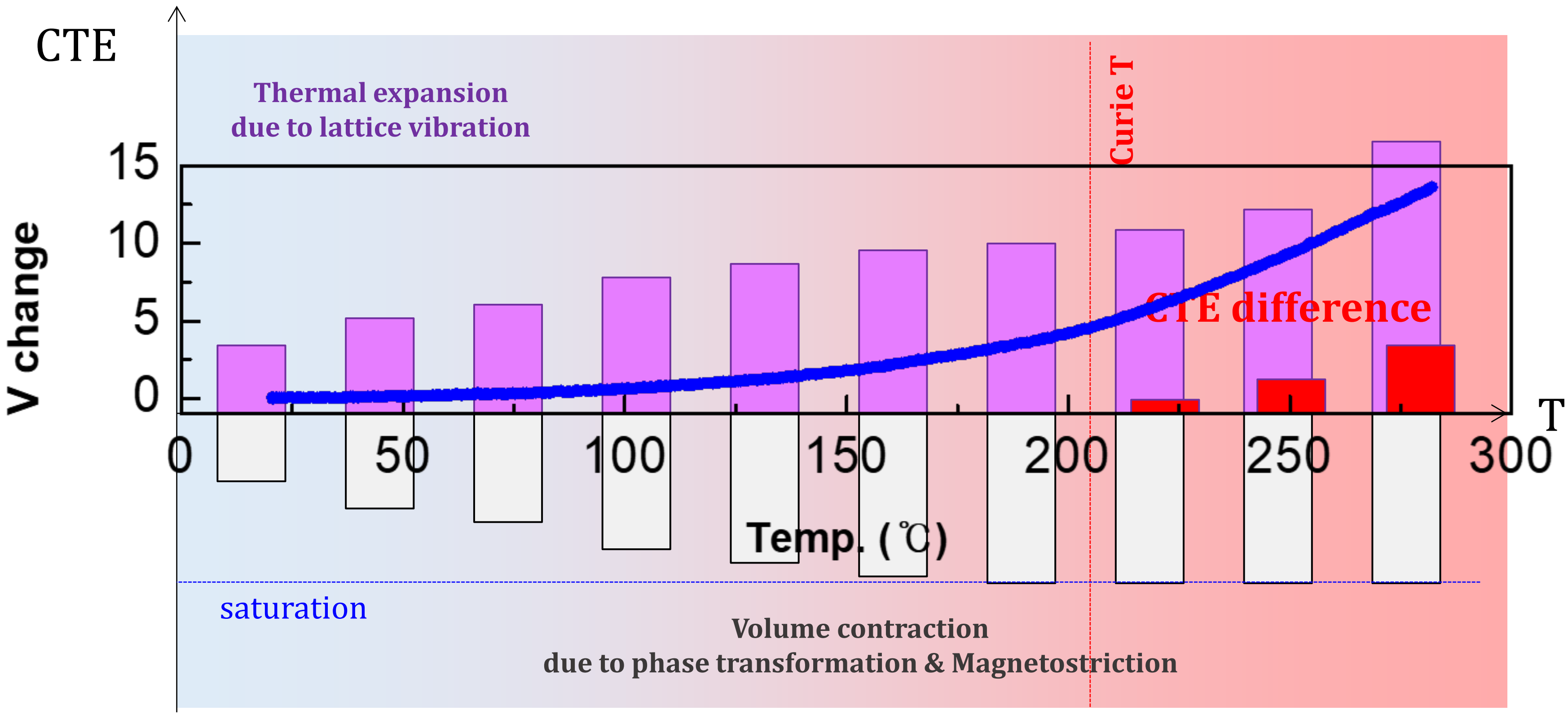
(1) Crystal structure; (2) lattice parameter (Å); (3) magnetic structure; (4) spin per atom (μ_B); (5) Curie or Néel temperature (°K).
γ_1, Fe–Mn and Fe–Ni; γ_2, Fe–Ni, Fe–Pt and Fe–Pd.



▶ **CTE is changed dramatically according to magnetic property**

- ✓ **γ_1 state is stable at low temperature, which can be easily changed due to small ΔE**
- ✓ **Invar effect is disappearing when the Ni-steel passes by the Curie Temperature**

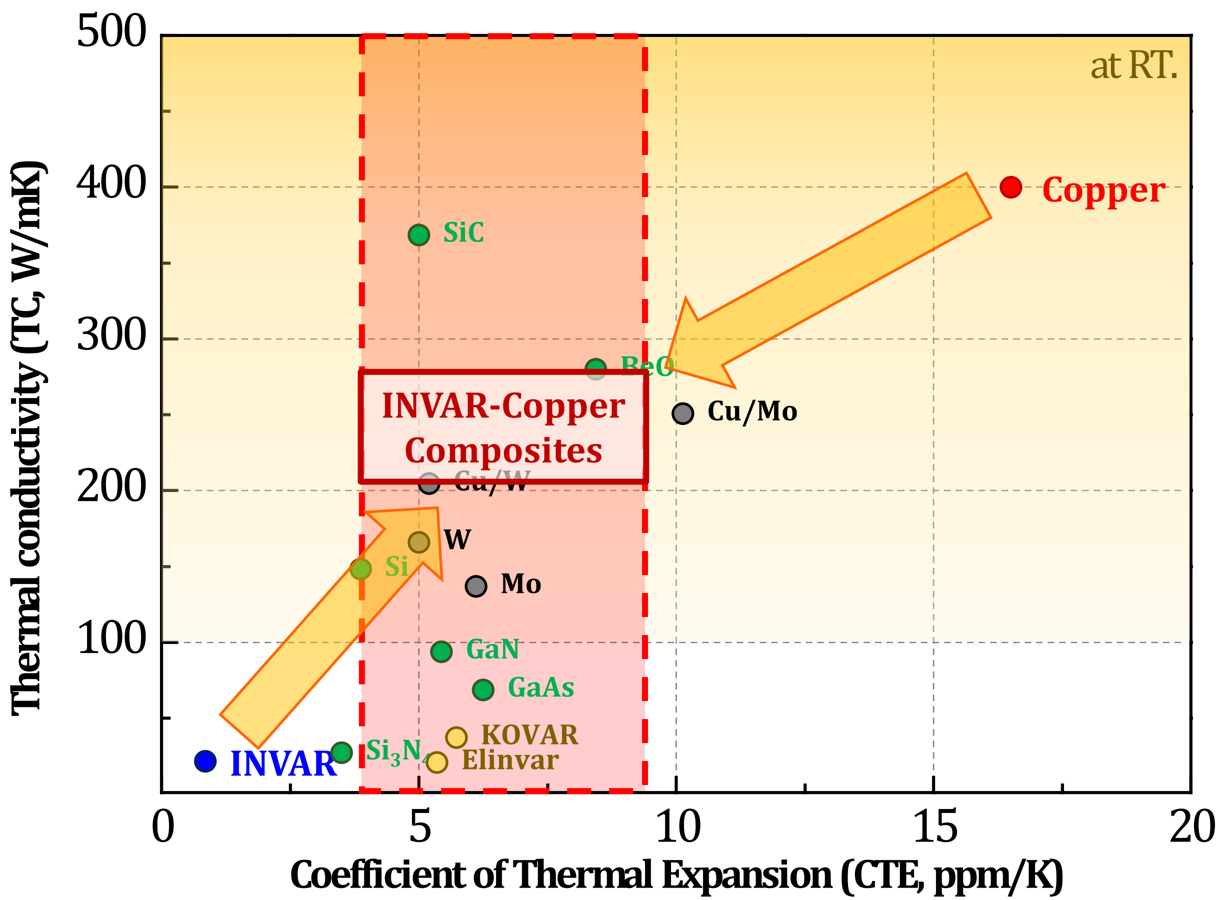
Schematic diagram of volume change of INVAR alloys



The INVAR effect, the combined effect of magnetostriction and magnetic phase transformation, cancels the volume change of lattice vibration out

How influence are the each factor ?

The composite of INVAR materials for heat radiation materials



재료	열전도도 (W/mK)	열팽창계수 (ppm/K)
Cu	**~ 385**	**~ 18**
Mo	~ 140	~ 6
W	~ 170	~ 5.5
Cu/Mo	~ 250	~ 10
Cu/W	~ 200	~ 5.5
Si	~ 150	~ 4
SiC	~ 370	~ 5
Si_3N_4	~ 20	~ 3.5
GaAs	~ 60	~ 6
GaN	~100	~ 5.5
BeO	~ 270	~ 8
INVAR	**~ 15**	**~ 1**
Super I.V.	~ 15	~ - 0.5
KOVAR	~ 20	~ 6.5
ELINVAR	~ 15	~ 5

저열팽창
INVAR (Fe-Ni)

방열 소재용 복합재료

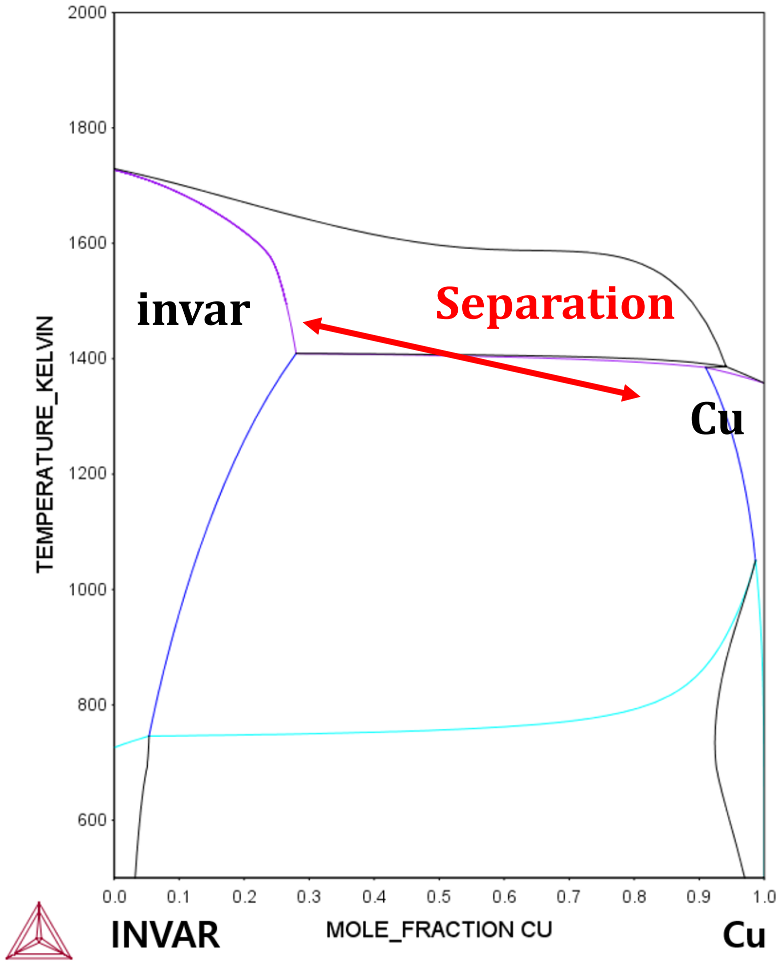
Mutual connection

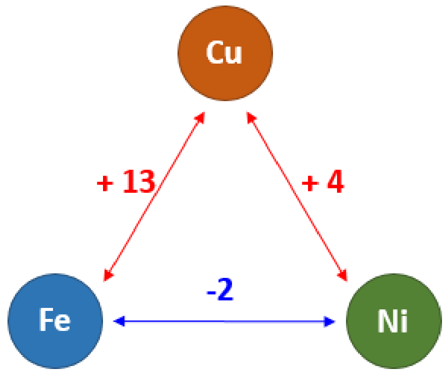
고열전도
Copper

Precedent studies

Fabricating INVAR-Copper composite by Arc-Melting (Casting)

Alloy design – thermodynamic calculation

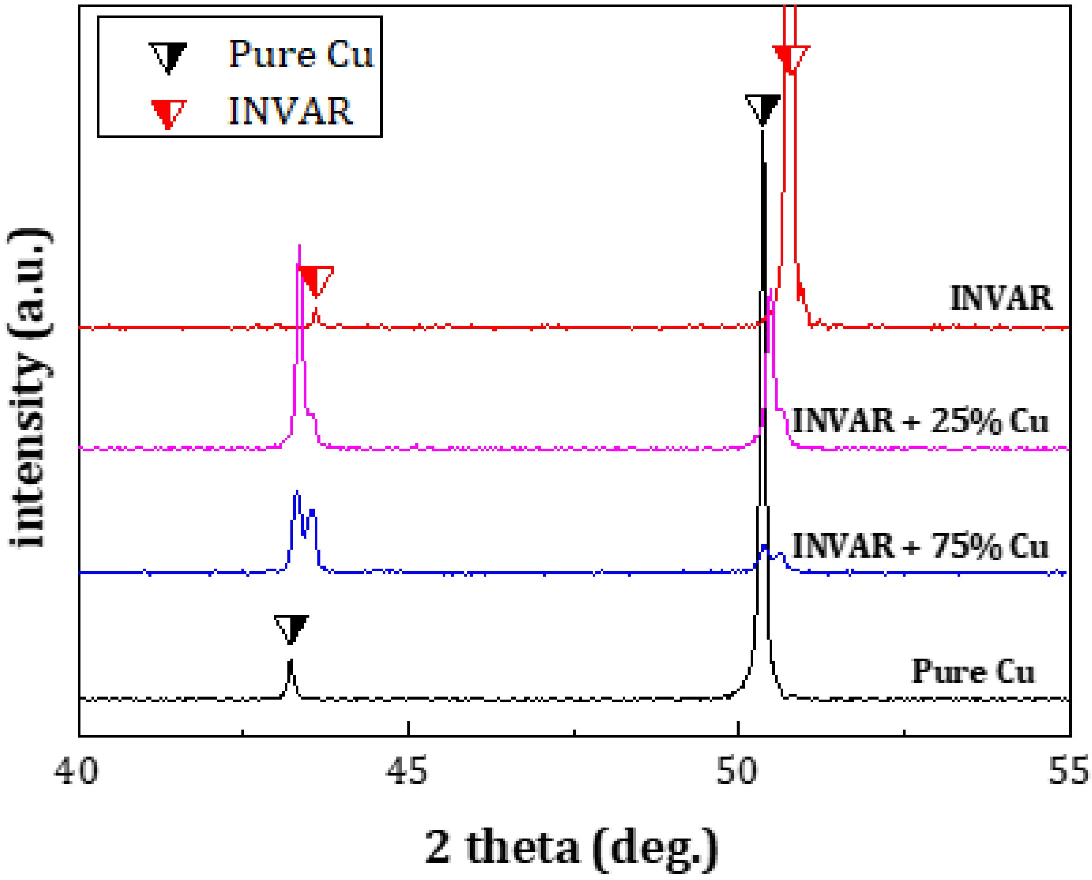


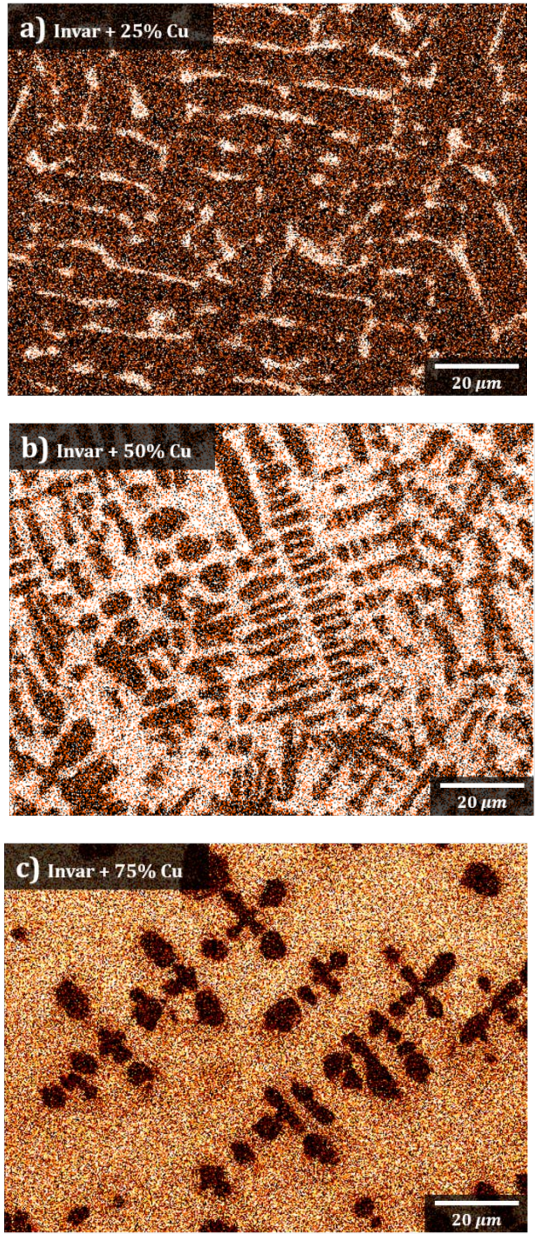


▶ **Copper-Invar composite can be fabricated through casting process**

- Using phase separation behavior of Copper and other elements

Arc-melting

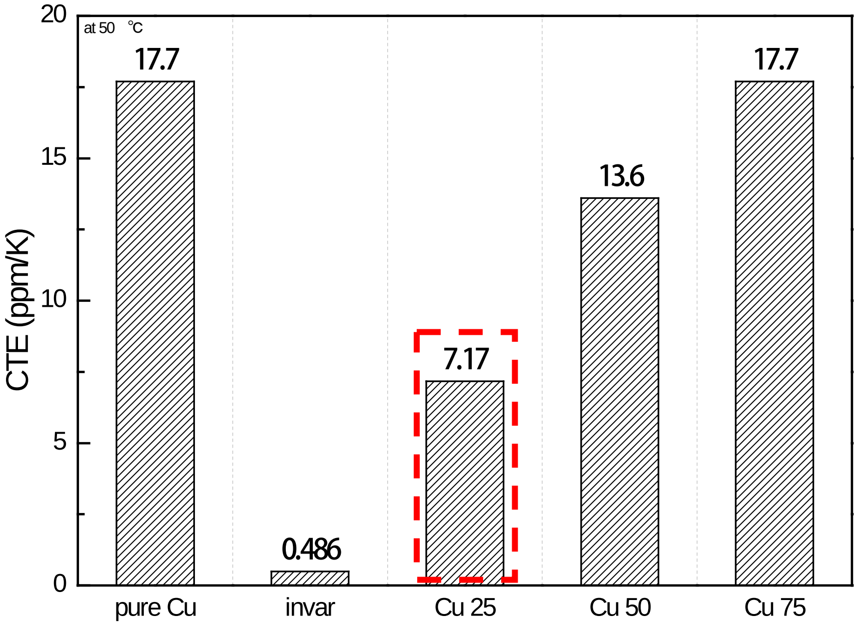


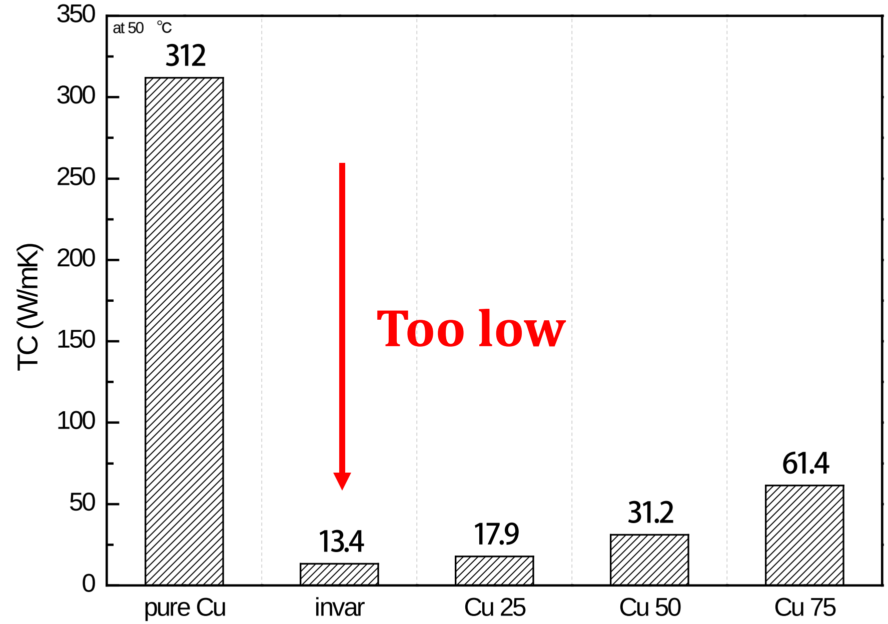


▶ **Invar can be phase separated with Cu like FCC HEA**

- Invar also shows dendritic growth

Property analysis



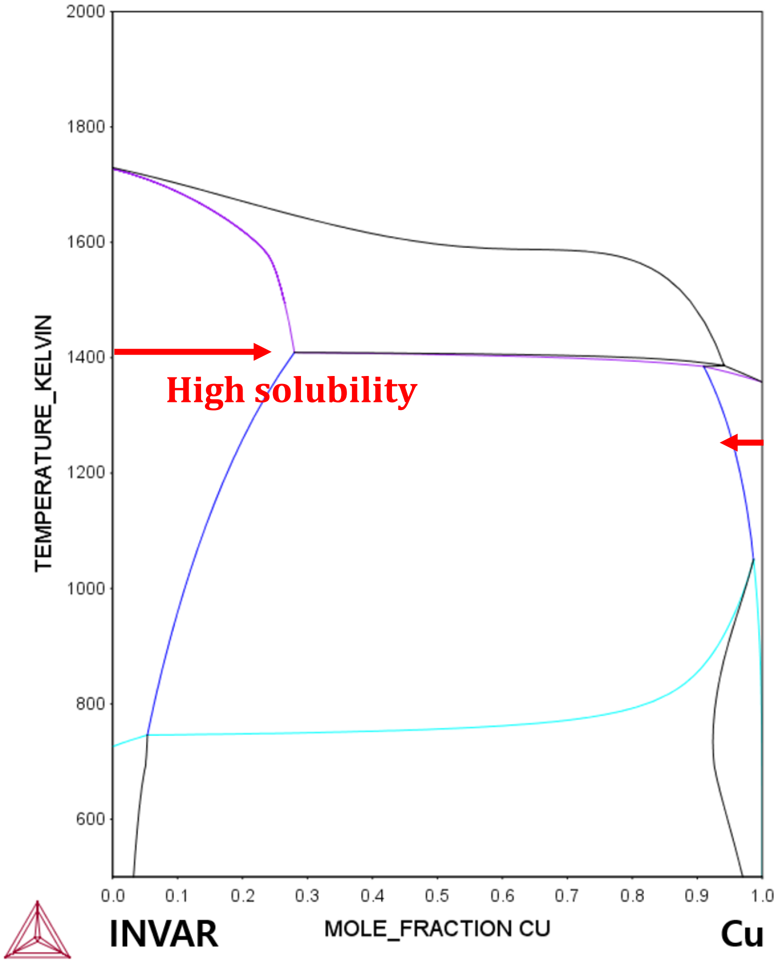


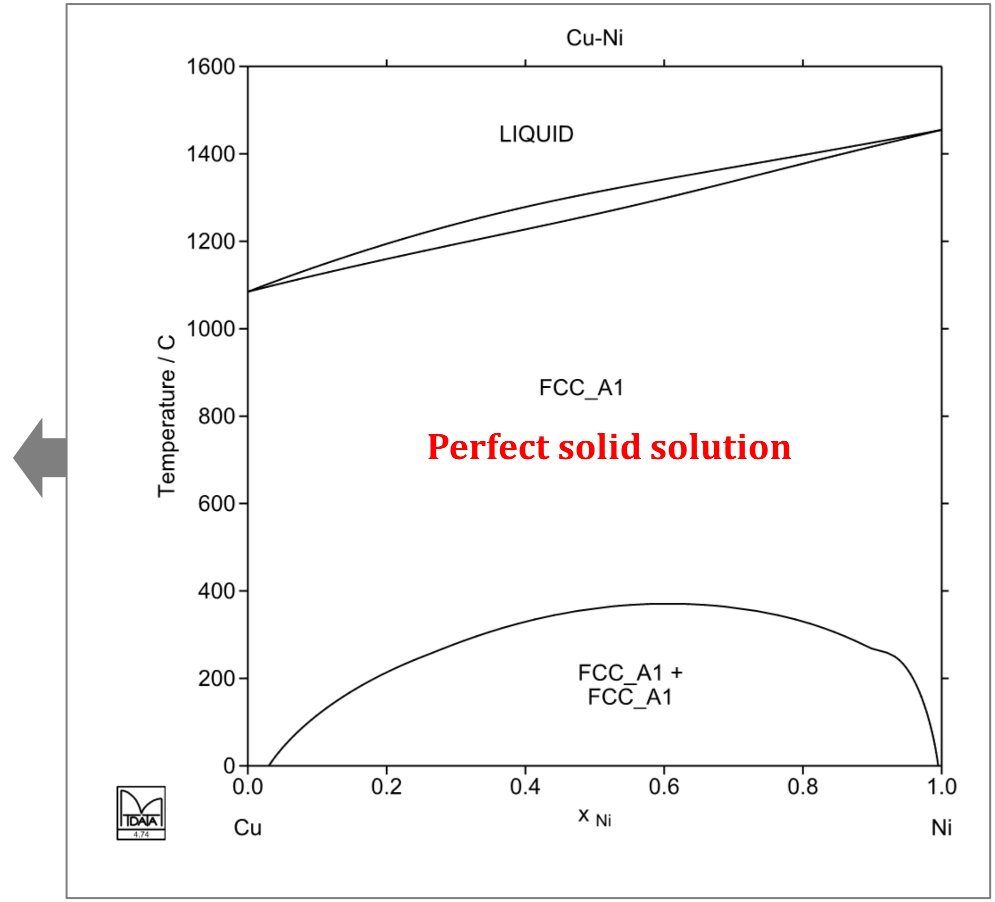
- **Thermal expansion coefficient**

1) Only 25% Cu meets required CTE value
2) CTE value increases linearly with increasing copper contents
3) It shows big difference with reference data - 40 at% Cu : ~8 / 47 at% Cu : ~9
→ This may be because of the difference on way of fabricating invar-copper composite

- **Thermal conductivity**

1) Any composition does NOT meet required TC value which were too low
2) And it shows also big difference with reference – 40 at% Cu : ~ 110





▶ **Copper-Invar composite can be fabricated through casting process**

- Using phase separation behavior of Copper and other elements

▶ **Problem : High solubility limit of Ni to Cu**

Approach

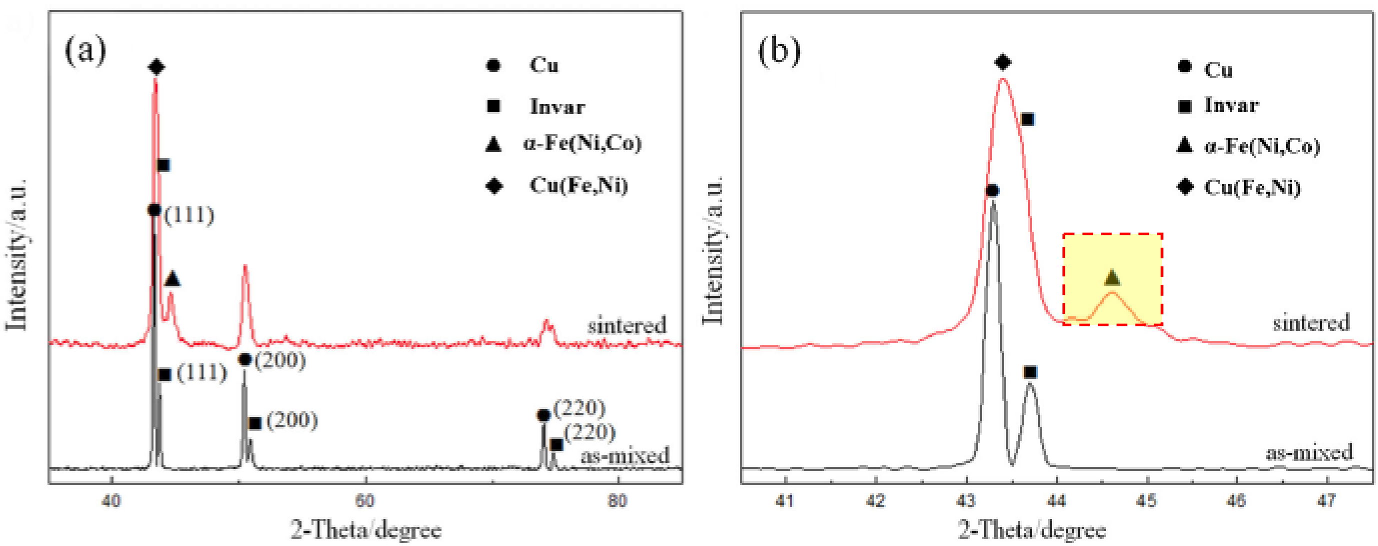
Fabricating INVAR-Copper composite by **SPS** (Powder metallurgy)

Preparation of Cu/Invar composites by powder metallurgy

D. Wu[1], S.-P. Wu[1], L. Yang[2], C.-D. Shi[2], Y.-C. Wu[3] and W.-M. Tang*[1,3]

An orthogonal experiment scheme was employed to study the influences of forming pressure, sintering temperature and holding time and Cu content on microstructure, hardness and electrical resistivity of the Cu/Invar composites prepared by the powder metallurgy (PM) technique. The interdiffusion of the Fe, Ni and Cu atoms of the composites during sintering was also investigated.
The results show t
content is 30 wt-%
structure of Cu for
the relative densi
resistivity of the co
of 600 MPa, sinter

Keywords: Powder metallur



1 Patterns (XRD) of Cu/Invar composites *a* after mixed and sintered (sample $A_1B_1C_1D_1$); *b* magnified region of *a* close to reflection angle $2\theta=42–46°$

Conclusion

1. Optimal PM Processing

Electrical resistivity : 1150C, 90min 50wt% Cu content

Thermal expansion : 1000C, 60min 50wt% Cu content

2. Invar alloy diffuse in Cu

Form Cu(Fe,Ni) solid solution

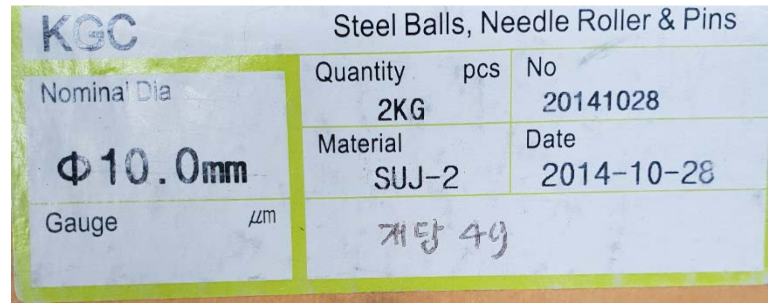
Invar alloy transforms Γ -> A

Process conditions – powder fabrication

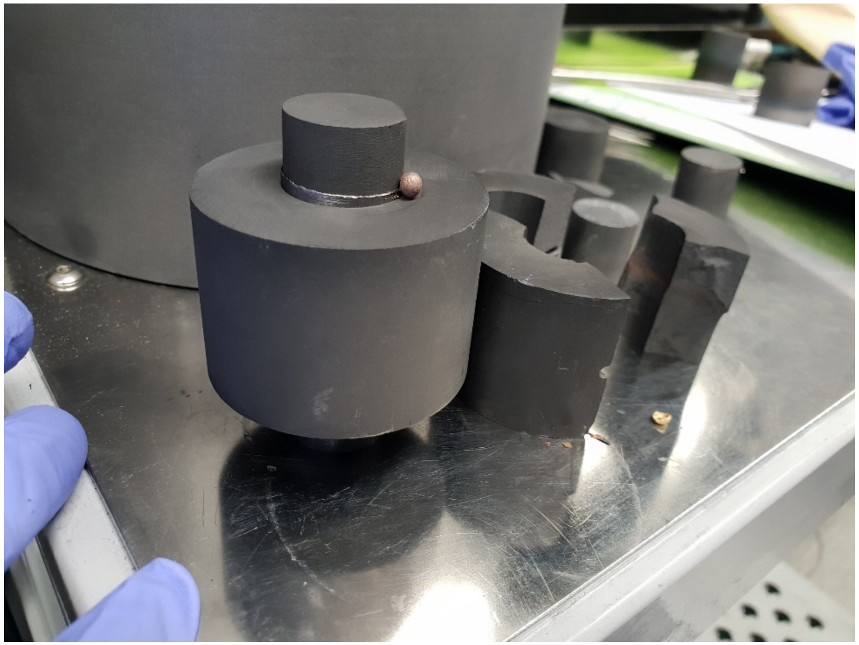
Grinding with **steel ball**

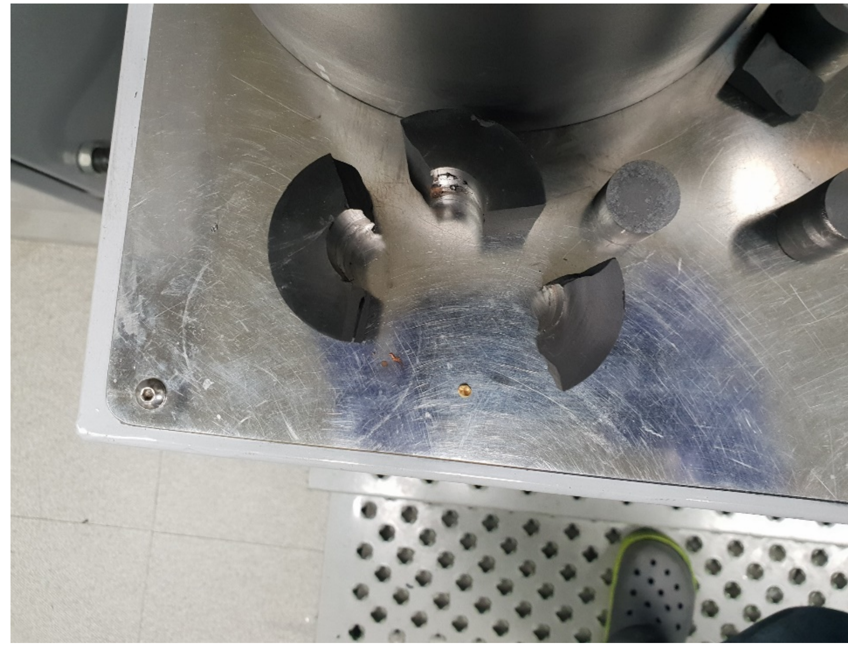
Cu -> ball coating (ductile)
Fe-Ni -> not grinding (hard)

Use commercial powder
Cu, Fe, Ni, Co



Process conditions – spark plasma sintering

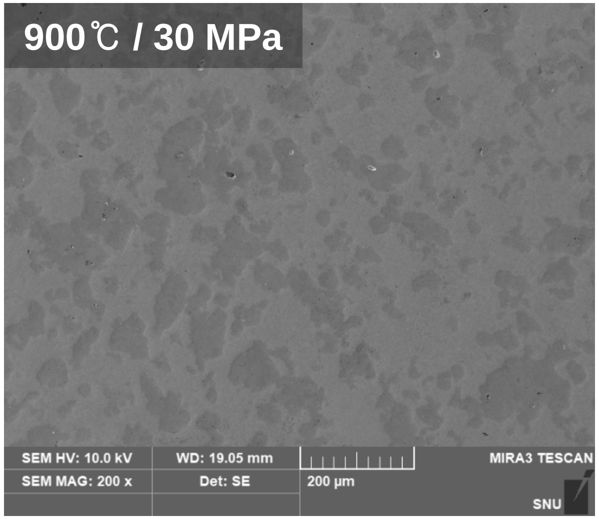


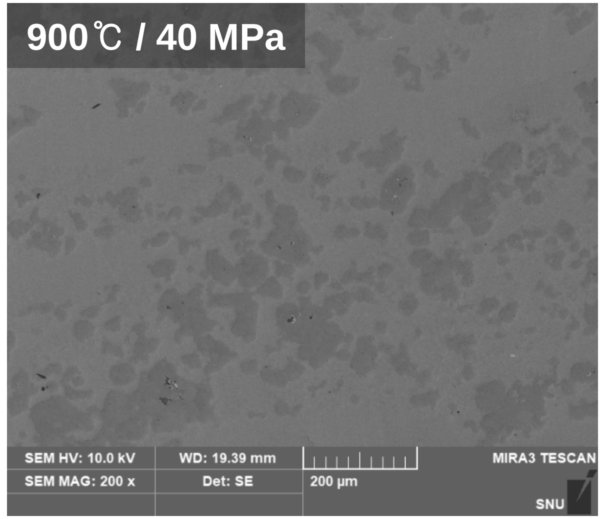


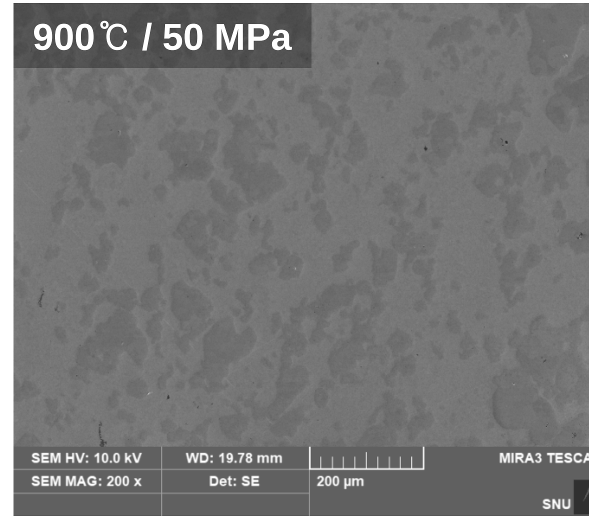
1000℃ sintering

	구분	조건 1	조건 2	조건 3	조건 4	조건 5
조성 (at.%)	Fe	32.57	32.57	32.57	32.57	32.57
	Ni	17.43	17.43	17.43	17.43	17.43
	Cu	50	50	50	50	50
시험 조건 (MPa, ℃)	압력조건	30	40	50	30	30
	온도조건	900	900	900	850	950

SEM analysis



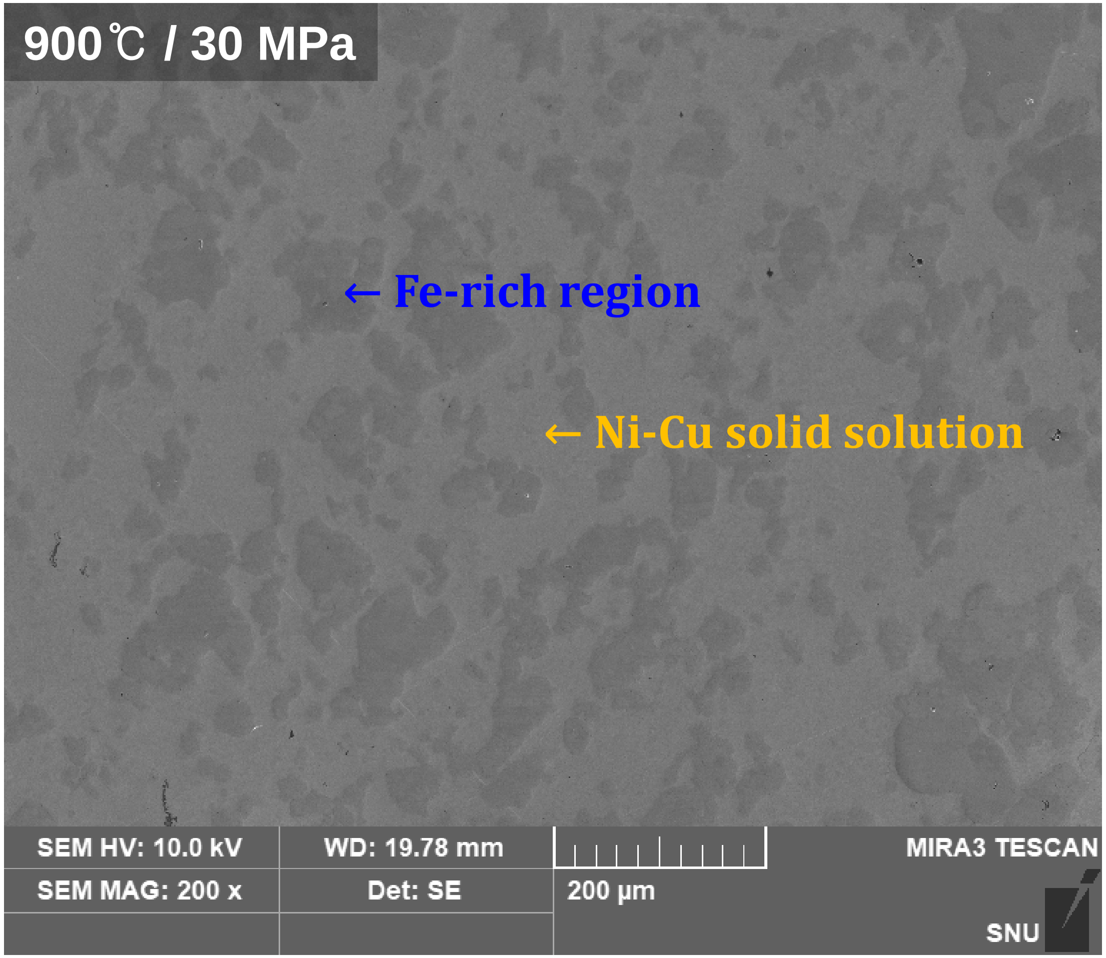


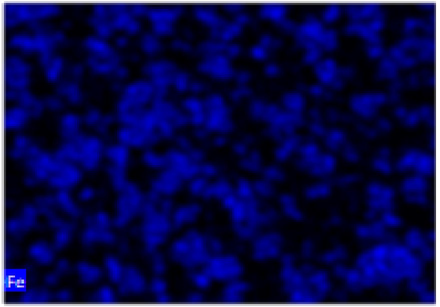


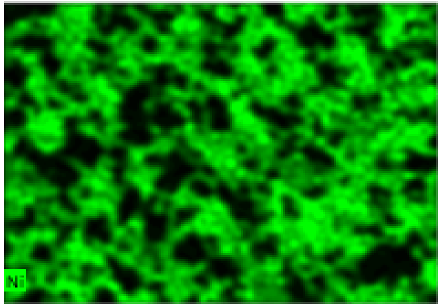
	조성 분석		조건 1	P=40	P=50	T=850	T=950
구분	Dark	크기(㎛)	~ 52.04	~ 44.69	~48.05	~42.05	~ 50.68
		분율(%)	~ 35.12	~ 30.09	~ 34.28	~ 33.64	~ 38.50

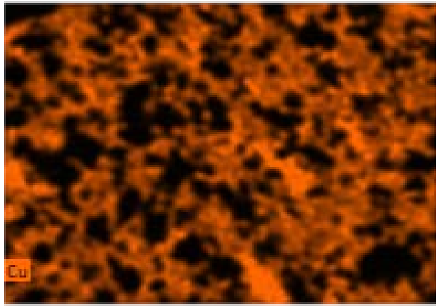
▶ **There was no big difference in size and fraction of segregated phase**

EDS analysis

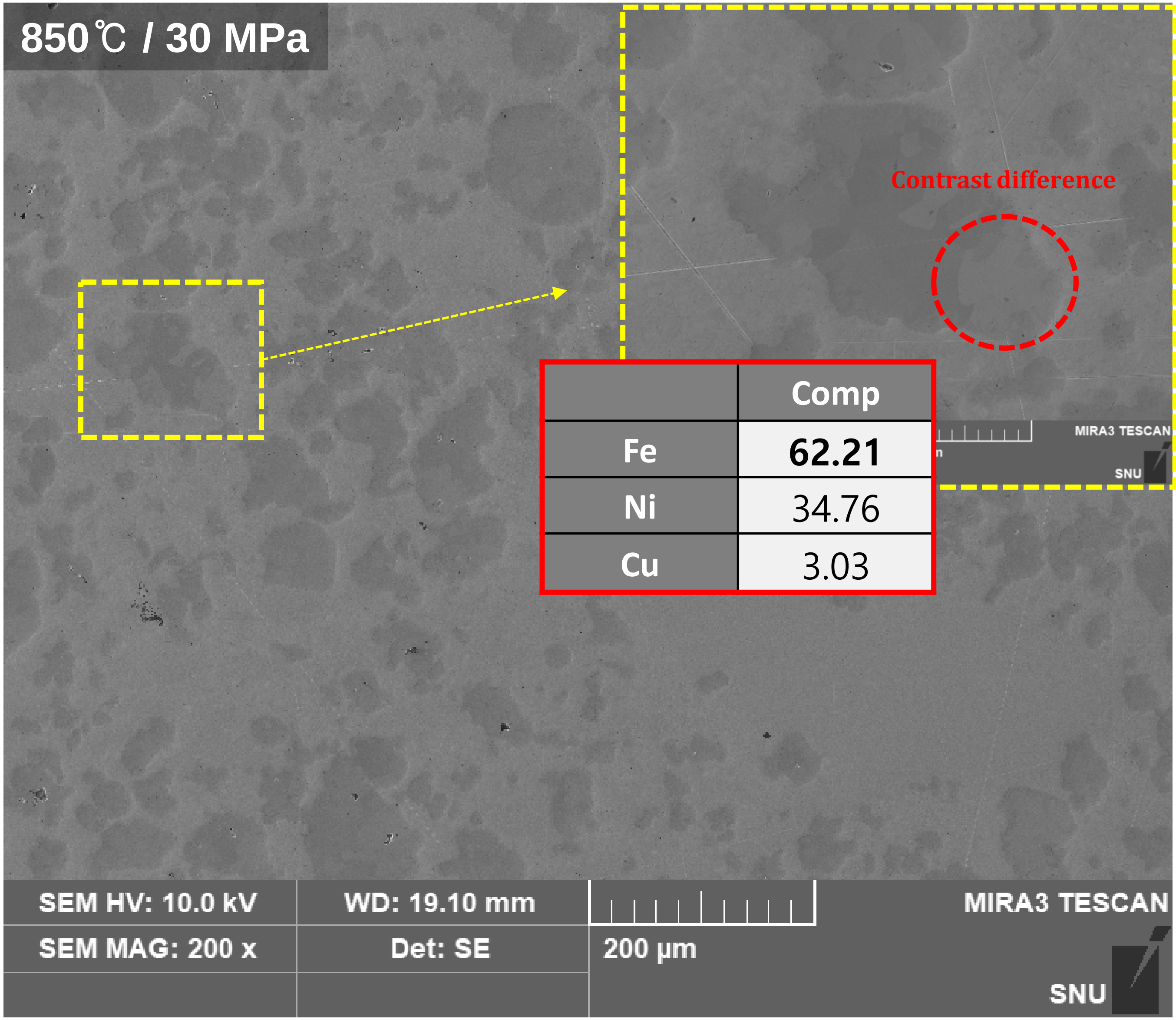








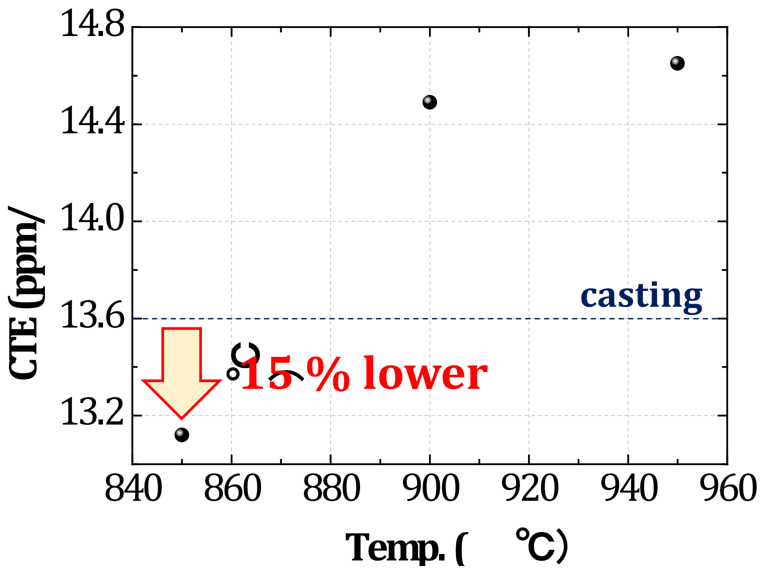
Dark	조성 분석	조건 1	P=40	P=50	T=850	T=950
조성 (at.%)	Fe	**98.84**	**97.36**	**99.09**	**89.50**	**98.60**
	Ni	0.62	1.52	0.58	**8.43**	1.05
	Cu	0.54	1.12	0.33	**2.07**	0.35

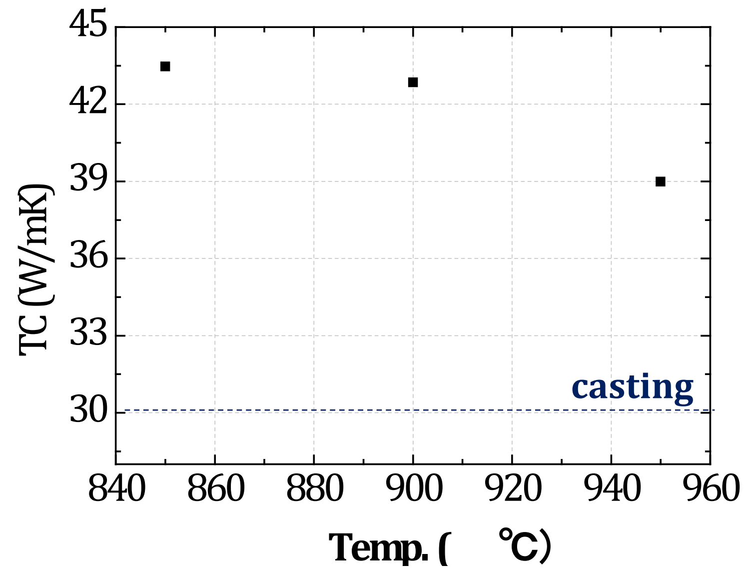


	Comp
Fe	**62.21**
Ni	34.76
Cu	3.03

▶ **Very small amount of INVAR was formed in Fe-rich region**

Process conditions – temperature control



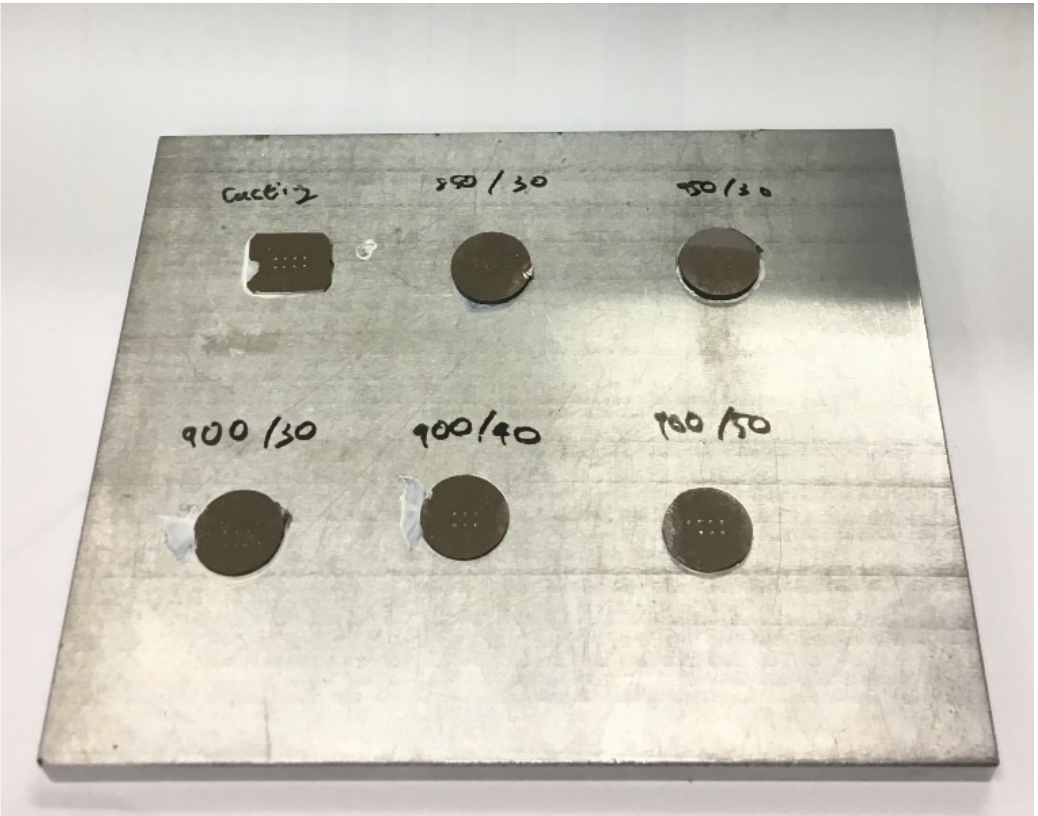


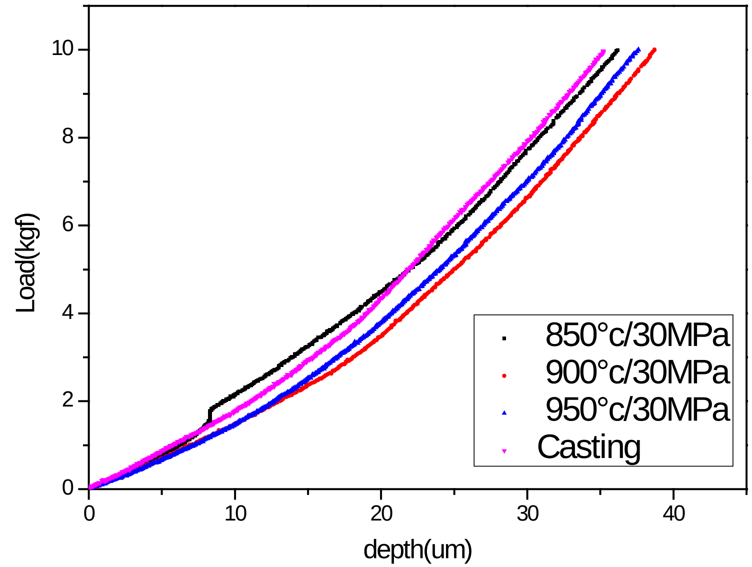
Increasing process temperature causes increase of CTE and decrease of TC

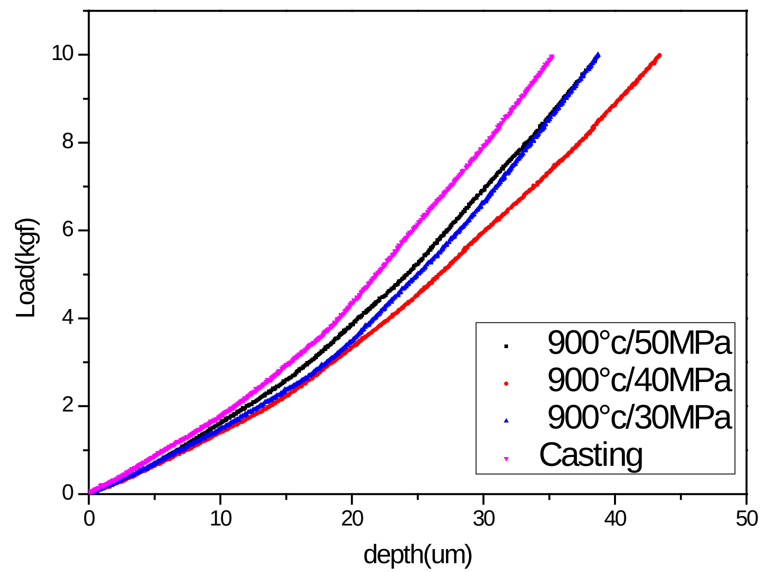
1. The alloy fabricated at 850C has 15% lower CTE than casted one
2. All of the samples have higher TC than casted one
3. For both properties, lower SPS temperature is favorable.

	TC	CTE
fe	71.9	12
ni	62.4	13
cu	401	17.7

Instrumented Indentation Test



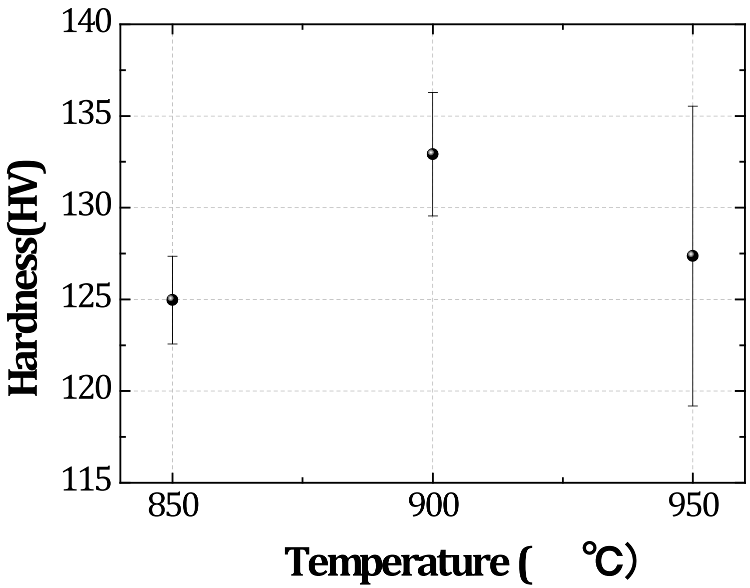


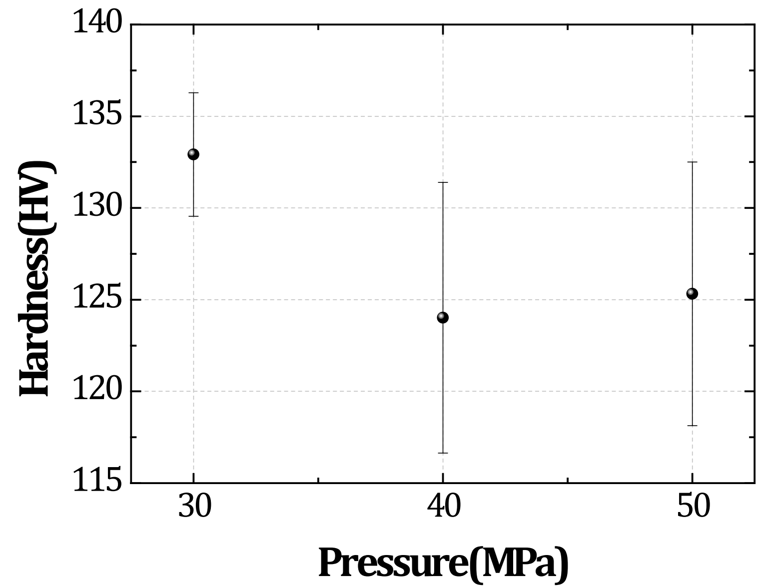


IIT (10 kgf load control) was conducted :

1. Since samples were too small to analyze, Reliable data could not be obtained by IIT
2. We only can attain the hardness of each sample

Vickers Hardness Results

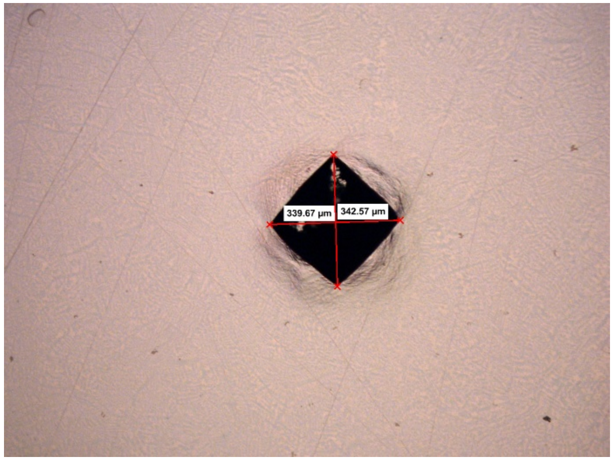




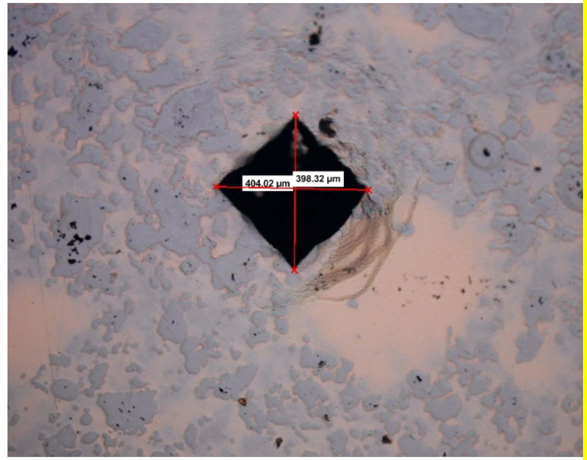
Condition	Average	STD
850°c/30MPa	124.96	2.40
900°c/30MPa	131.15	1.76
950°c/30MPa	127.36	8.18
Casting	156.66	1.93

Condition	Average	STD
900°c/30MPa	131.15	1.76
900°c/40MPa	124.01	7.38
900°c/50MPa	125.31	7.18
Casting	156.66	1.93

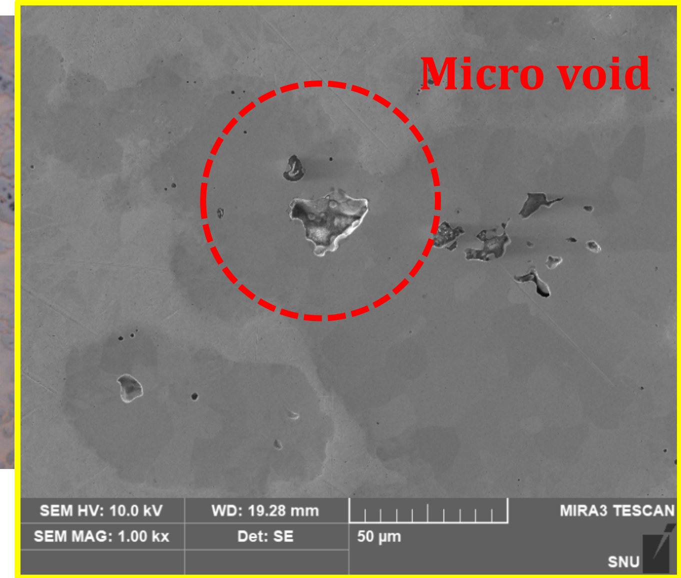
▶ **Samples fabricated at much harsh conditions have large STD than the others**

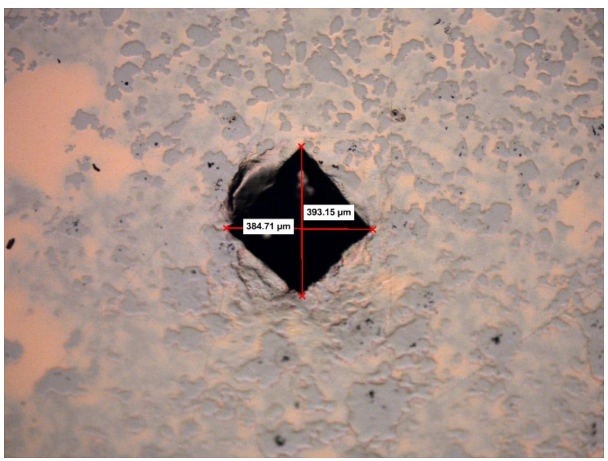


Casting

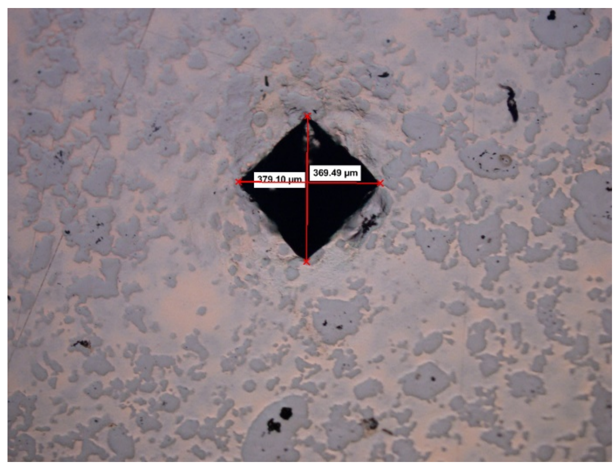


900°c/40MPa

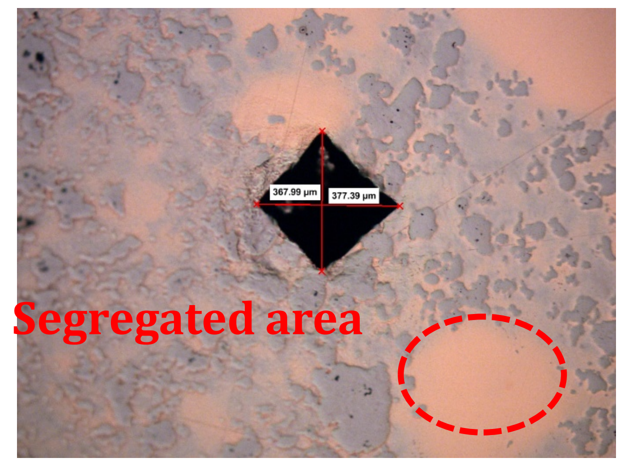




850°c/30MPa



900°c/30MPa



950°c/30MPa

▶ **Since these samples have weak interphase due to voids and large segregation regions**

Summary and Conclusion

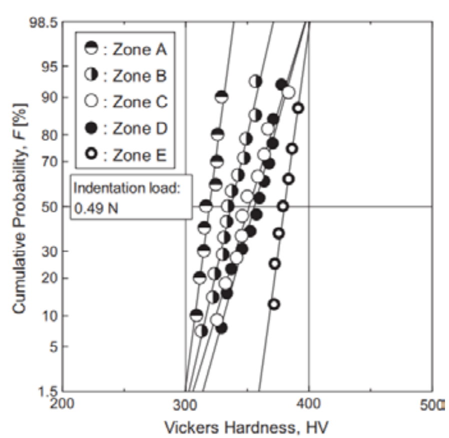
Fatigue strength prediction for inhomogeneous face-centered cubic metal based on Vickers hardness

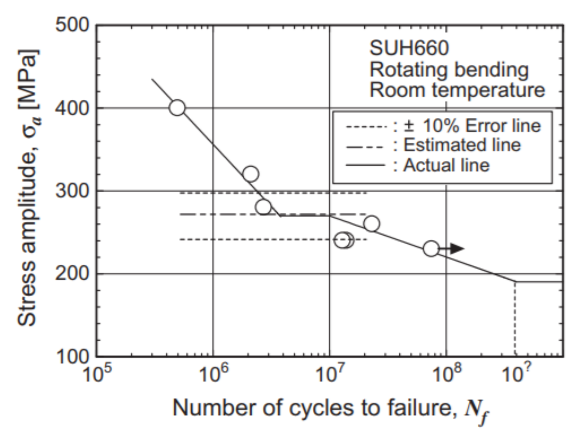
Hao Wu [a], Shigeru Hamada [b,c,d,*], Hiroshi Noguchi [b,c]

[a] Department of Mechanical Engineering, Graduate School of Engineering, Kyushu University, 744 Moto-oka, Nishi-Ku, Fukuoka 819-0395, Japan
[b] Department of Mechanical Engineering, Faculty of Engineering, Kyushu University, 744 Moto-oka, Nishi-Ku, Fukuoka 819-0395, Japan
[c] Research Center for Hydrogen Industrial Use and Storage (HYDROGENIUS), National Institute of Advanced Industrial Science and Technology (AIST), 744 Moto-oka, Nishi-ku, Fukuoka 819-0395, Japan
[d] International Institute for Carbon Neutral Energy Research (WPI-I2CNER), Kyushu University, 744 Moto-oka, Nishi-ku, Fukuoka 819-0395, Japan

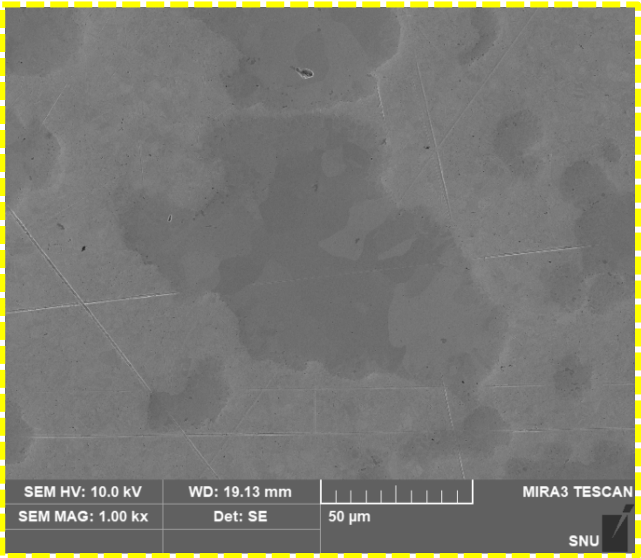
A B S T R A C T

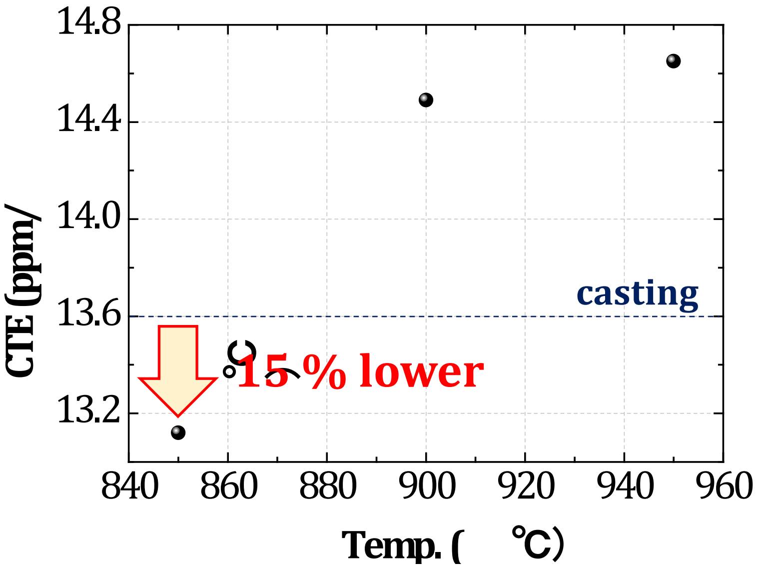
To find the Vickers hardness (*HV*) value for predicting the fatigue strength of inhomogeneous face-centered cubic (FCC) metals, *HV* tests were performed on SUH660 stainless steel. The results indicate that the intrinsic hardness distribution can be obtained from the *HV* distribution in test zones according to the Vickers hardness definition. The soft zone greatly affects the fatigue strength of an inhomogeneous FCC metal. Therefore, for another inhomogeneous FCC metal in which fatigue cracks initiate and propagate easily in the softest zone, the fatigue limit can be predicted using the mean *HV* value of the softest zone.





Summary





1. We fabricated INVAR-copper composite by spark plasma sintering(SPS) process to control the solubility of nickel into copper under several conditions
2. Phase separation was aroused not into INVAR & Cu, but into Fe & Cu-Ni solid solution
3. We only can obtain INVAR at the lowest SPS temperature : 850 ℃
4. If we move on to harsh conditions such as high P or T, more micro-size void was formed
5. In that sense, samples formed in harsh conditions shows large deviation of their hardness

Thank you for your kind attention