Structure and properties of invar alloys for MIM technologies

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Abstract. The paper studied Fe-Ni alloys obtained by sintering from mixtures of powders. Powders with 30-40 wt. % Ni were mixed with paraffin and wax binder and then pressed and sintered at 1300 °C during 1 hour. It has been shown that the face centered cubic lattice (γ-phase) and body centered cubic lattice (α-phase) are formed after sintering of powders mixture. The content of the α-phase decreases from 37 % to 2 % with increase of Ni concentration from 30 to 35 wt. % Ni in powders mixture. The average grain size of the γ-phase decreases from 26.5±12.3 μm to 18.3±9.1 μm, and porosity of samples increases from 13±1.4 % to 18.4±1.1 %. The lattice parameter of the γ-phase increases from 3.5849·10⁻¹⁰ m to 3.597·10⁻¹⁰ m and it corresponds to well-known invar alloys. The maximum value of the microhardness of sintered samples is 1.04±0.07 GPa. Thus, alloys obtained by sintering of Fe and Ni powders mixtures has an invar properties typical of cast alloys.

1. Introduction
One of the most important strategic trend for the development of Siberia and the Arctic is the creation of new materials. Accordingly, there is a need to develop new materials and technologies for their manufacture with specific mechanical or functional properties. Fe-Ni alloys with low coefficient of thermal expansion (CTE) [1, 2] has demand for the application in the field of high precision devices such as optoelectronic or light wave communication systems, housing or structural components [3]. There are different methods for obtaining of invar alloy (iron-nickel alloy), but powder metallurgy (PM) presents several processing advantages as compared with casting method.

Metal injection molding (MIM) is one of the main effective methods for fabrication of product with complex geometry [4]. Usually, it uses Fe-Ni alloy particles obtained by evaporation and cryo-condensation process and the gas-phase method [5-7] for realization of this technology, but these technique is rather expensive for obtaining of alloy powders. Powder metallurgy allows obtaining alloys with different composition by sintering from powders mixtures; however, there are not enough studies of invar alloys sintered from powders mixtures. Nevertheless, these studies are important for 3D-printing and MIM technologies.

The aim of this paper is to study structure and properties of alloys obtained by sintering from powders mixtures which can be used for MIM technologies.
2. Material and methods
The Fe-Ni mixtures of iron and nickel powders were used, the nickel content varied from 30 to 40 wt. %. The preparation of samples was carried out on several steps [8]. First of all, it was prepared binder that consists of paraffin and wax in a ratio of 90:10 which was mixed for 10 min. After this, the metal powder was added to binder, mixed for 30 min and this mixtures were uniaxial pressed. The samples were sintered in a vacuum furnace; the sintering temperature was chosen according to the phase diagram of the Fe-Ni alloy and was 1325 °C in 1 hour, heating rate was 5 °C min⁻¹, before sintering process samples were hold at 200 °C where binder was removed during one hour of holding time. The samples were etched with a solution of one part nitric acid in 20 parts ethanol [9].

The average grain size of the γ-phase and porosity of the finished MIM-specimens was studied by light microscopy (Labomet-I, Russia). The phase identification was investigated by the X-ray diffraction (XRD). XRD measurements were carried out using a difractometer with Co Kα radiations (Kα = 1.7902 Å). X-ray patterns were obtained using step-by-step method with statistics accuracy better than 0.5 %. XRD line profile analysis was used to determine the coherently diffracting domain (CDD was calculated by the Scherrer equation [10] for the lines (111)) and microdistortion (calculated according to the Stokes – Wilson equation [11] for the lines (311)). The lattice parameters were calculated with extrapolation on cos²θ values [12] using all lines. Finally, the microhardness of the samples was obtained by a Vickers indenter with a load 1.0 N (PMT-3M, Russia).

3. Results
X-ray patterns and phase identification are shown in Fig. 1. It is revealed that the matrix of the alloys were composed of austenite γ-phase (face centered cubic lattice, FCC), which corresponds to the formation of invar alloy. Small peaks corresponding to body centered cubic lattice (BCC, α-phase) crystal structure appeared in the diffraction patterns for samples with Ni contain (30 – 35wt. %), probably due to relatively large size of powders; it coincides with the literature data [6]. The peak intensity corresponding to the BCC phase was decreased with increase of Ni content (Table 1). An extrapolation of this dependence to the zero intensity allows to obtain a limit of existence BCC-phase, equals 34.8 %.

![Figure 1. X-ray patterns and phase identification of samples](image_url)

The structure of samples with 30 wt. % Ni (a) and 40 wt. % Ni (b) are shown in Fig. 2. As one can see clear austenitic microstructure with typical austenite twins was formed. The presence of α-phase is detected by light microscopy after etched of samples (Fig. 2, a – black area). The average grain size of the austenite decreases from 26.5±12.3 μm to 18.3±9.1 μm with increasing of Ni content from...
30 wt.% to 40 wt.%. The porosity of samples increases from 13 ± 1.4 % to 18.4 ± 1.1 % with increasing Ni content.

Table 1. Phase composition of Fe-Ni compacts sintered at 1325 ºC

| The content in the mixture of Ni, wt. % | Relative content of phase, % (determined by sums of the integral line intensities) |
|--------------------------------------|---------------------------------------------------------------------------------|
|                                      | FCC                        | BCC                        |
| 30                                   | 63                         | 37                         |
| 32                                   | 90                         | 10                         |
| 35                                   | 98                         | 2                          |
| 37                                   | 100                        | 0                          |
| 40                                   | 100                        | 0                          |

The lattice parameters of γ-phase depending on the nickel content in sintered samples are shown in Fig. 3. One can see that the lattice parameters increase up to 37 wt. % of Ni and almost does not change for more content of Ni. It is in a good agreement with literature data [13].

The CDD of γ-phase is 50±5 nm and does not significantly change with increasing nickel content. The microdistortion of the crystal lattice of γ-phase changes from 1.9±0.15·10⁻³ to 1.3±0.13·10⁻³ with an increase of the nickel content, this may be associated with the disappearance of the α-phase in the alloy.

The dependence of microhardness ($H_{μ}$) of Invar alloys for different Ni content is shown in Fig. 4. It is shown, that $H_{μ}$ of sintered samples changes non-monotonous for different Ni content, $H_{μ}$ increases from 1.04±0.07 GPa to 0.78±0.05 GPa, after $H_{μ}$ increases to 1.03±0.09 GPa. The first stage could be associated with α-phase; a second stage is connected with porosity and grain size of γ-phase. The $H_{μ}$ value for Invar 36 [14] is 1.3 GPa and depends on a porosity and grain size of γ-phase for samples obtained by metal injection molding technology.
4. Conclusion

It has been shown that after sintering of Fe and Ni of powder mixtures were formed a face centered cubic structures with small amount of BCC phase. Content of $\alpha$-phase depends on Ni concentration and changes from 37 % to 2 %, and disappear at 34.8 wt. % of Ni. The average grain size of the $\gamma$-phase decreases with increase Ni content from 26.5±12.3 $\mu$m to 18.3±9.1 $\mu$m, and porosity of samples increases from 13±1.4 % to 18.4±1.1 %. The lattice parameter of the $\gamma$-phase depends on content of Ni and increases from $3.5849 \times 10^{-10}$ m to $3.597 \times 10^{-10}$ m which correlates well with literature data. It has been shown the microhardness of sintered samples changes non-monotonous with increase of Ni content, the maximum value is 1.04±0.07 GPa.

Acknowledgement

This research was funded by Russian Foundation for Basic Research and the government of the region of the Russian Federation, grant № 18-48-700039 and in the framework of the Program of increasing the competitiveness of TSU.

References

[1] Guillaume C E. 1897 C R Acad Sci 125, 235–238.
[2] Maslyuk V A, Panasyuk O A, Vlasova O V. 2003 Powder Metall. Met. Ceram. 42 536–539
[3] Lin C-T, Chio S-B, Chi S. 2006 IEEE J. Sel. Top. Quantum Electron. 12(5) 970–982.
[4] Cha B, Jang J M, Lee W et al. 2012 J. Ceram. Process. Res. 13, 22–25.
[5] Duhamel C, Champion Y et al. 2005 J. Alloys Compd. 393, 204–210.
[6] Hidalgo J, Jiménez-Morales A, Barriere T et al. 2014 Powder Metall. 2, 127–136.
[7] Oglezneva S A, Saenkov K L, Grevnov L M. 2017 Vestnik PNIPU 3, 34–48.
[8] Dovydenkov V A, Krys’ M A, Fetisov G P. 2006 Zagotovitel’nyye proizvodstva v mashinostroyenii. 8, 47–50.
[9] Luong D D, Shumugasamy V C, Gupta N et al. 2015 Mater. Des. 66 516–531
[10] Scherrer P. 1918 Göttinger Nachrichten Gesellschaft 2 98–101.
[11] Stokes A R, Wilson A J C. 1944 Proceedings of the Physical Society. 174–181.
[12] Pramanick A, Omar S, Nino J C et. al. 2009 Appl. Crystallogr. 42(3) 490–495.
[13] Chamberod A, Laugier J, Penisson J M. 1979 J. Magn. Magn. Mater 10 139–144.
[14] Cubberly W H, “Properties and selection – nonferrous alloys and pure metals”, in ASM Metals