Development of Fe-20Cr-5Al-1Y2O3 ODS alloy with addition of Ni by means of Arc plasma sintering (APS) method

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Abstract. APS has two main advantages over the conventional method since it reduces the energy consumption and process time significantly. In this work, ODS alloys composed of Fe-20Cr-5Al-1Y2O3 with addition of 0.5, 1, 1.5, and 2 wt% nickel were produced. These alloys are firstly fabricated via powder metallurgy method consisting of mechanical alloying by high energy milling for 8 hours and uniaxial isostatic pressing with 20 ton-force/in2 pressure, and subsequent sintering in APS for 28 minutes. The alloy samples were investigated using Scanning Electron Microscope (SEM) equipped with X-Ray Diffraction Spectroscopy (EDX) to reveal the microstructure and chemical composition, X-Ray Diffraction (XRD) to analyze the phases which occur after sintering, and Vickers micro hardness testing to examine the hardness value of specimens. The results show that APS method in processing ODS alloy has given two main technical advantages over the conventional method: first, low energy need, and second, short process time. The addition of nickel leads to the formation of the microstructure consisting of three main phases, the (Fe,Ni) or kamacite, NiAl and ferrite matrix. The presence of NiAl is recognized as essential since it can improve oxide particles within the alloy matrix and along grain boundaries to impede dislocation motion particularly at high temperature (creep). Nickel addition also shows increasing hardness value of the ODS alloys.

1. Introduction
Oxide Dispersion Strengthened (ODS) alloy is a kind of alloy which consists of high temperature matrix phases such as Fe-Cr, Fe-Al, Fe-Cr-Al, Ni-Cr or Ni-Al and small addition of oxide particles, which give the alloy sufficient resistance to corrosion or oxidation at high temperature applications, such as nuclear applications [1-4]. ODS alloy is fabricated by mechanical alloying method using milling process, in which cold welding, fracturing and re-welding can occur. Both cold welding and re-welding are actually the same process, the difference is located in the milling stages. Cold welding occurs when milling is in progress because of the collision between particles of powder at room temperature (without heating process) while re-welding happens as powder inside HEM-E3D tool collide with each other and make the particles of powder separated (fractured) but at the end it will merge again (re-weld process) [5, 6]. Then, the mixed powder is pressed, as the result of the powder stick to each other (more compact/denser). It will make the sintering process easier, which means less energy consumption, because the gaps between particles are close that will maximized the necking process. After that conventional sintering process was used but requires long processing time to reduce the porosity.
significantly and consumes a high energy. As an alternative way producing ODS alloys is sintering with plasma in APS which is developed in the Center for Science and Technology of Advanced Materials (PSTBM)-BATAN. It has been proved to reduce sintering energy and time significantly.

In this study, a new ODS alloy based on FeCrAl with addition of nickel was developed using APS method. Nickel is assumed to act as a strengthening element in super alloys and improves their creep and oxidation resistance. Microstructure, mechanical properties, and phase formation were investigated using electron microscopy and X-ray diffraction to get detailed insight into the effectiveness of addition Ni in ODS alloy.

2. Experimental

ODS alloy samples are fabricated from powder materials with compositions and particle sizes as shown in Table 1.

| Element | Weight percentage | Size  |
|---------|-------------------|-------|
| Fe      | Bal               | 5 µm  |
| Cr      | 20 %              | 5 µm  |
| Al      | 5 %               | 20 µm |
| Y2O3    | 1 %               | 50 nm |
| Ni      | 0.5 %, 1%, 1.5%, 2%| 10 µm |

The materials were mixed and milled using high energy milling (HEM-E3D) from Nanotech Indonesia for 8 hours in order to reduce the particle size and for homogenization, followed by isostatic pressing 20 ton-force/in² using AKS 3030 pressing tool to produce green body as sample coins. The sintering process was conducted using APS method at 12 V and 80 Amps DC current in Argon atmosphere up to 28 minutes. JEOL SEM-EDX was used to observe the microstructure of the samples at magnification as high as 5000x, and to identify the chemical composition. Determination and identification of new phases which occur in the sample are investigated using RIGAKU-SMARLAB X-Ray Diffraction (XRD). The result was then analyzed and refined with Xpert HighScore software. Vickers microhardness test was performed to examine the relation of nickel addition to alloy hardness. The test was conducted with 300 grams load and 10 seconds indentation time.

3. Results and discussion

3.1. Microstructures

SEM observation of the sample alloys containing 0.5 and 2 wt% Ni after sintering in APS for 28 minutes are shown in Figure 1.

SEM images of the samples containing 0.5 and 1 wt% Ni in Figure 1 generally show an alloy with large and small grains containing porosities (appear as black) spread in grains and grain boundaries. The fraction of porosities to observable area is about 10%. This is quite good, which indicates that although the APS method uses a relatively short process time and pressing is absent during sintering, it can significantly reduce the size and amount of porosity, which is in agreement with the investigation of Kumar et al. [7]. The reason for this is the difference in diffusion rate between the phase formation and the necking process during sintering [8].

The effect of nickel variation on the microstructure of ODS alloy sample cannot be identified in the Figure 1. No change of the microstructure and the number of the porosity on the specimens was observed. This can suggest that the powder metallurgy preparation process prior to sintering has successfully homogenized the powder mix and make the samples more compact after pressing.
Figure 1. SEM micrographs of Fe-20Cr-5Al-1Y₂O₃ with addition of (a) 0.5 and (b) 2 wt% Ni sintered in APS for 28 minutes.

Table 2. Chemical composition of ODS alloy measured by EDX at position as indicated in Figure 1.

| ODS Steel | No | Fe  | Cr  | Al  | Ni | Y   | O   |
|-----------|----|-----|-----|-----|----|-----|-----|
| Fe        | 1  | 26.8| 10.3| 9.7 | -  | 30.6| 22.5|
| Ni 0.5%   | 2  | 28.7| 58.8| 2.4 | -  | 0.7 | 2.7 |
|           | 3  | 64.9| 17.7| 7.3 | -  | 1.2 | 8.8 |
| Ni 2%     | 1  | 22.8| 7.1 | 2.7 | -  | 16.2| 51.2|
|           | 2  | 23.2| 9.3 | 9.6 | -  | 20.8| 37.2|
|           | 3  | 69.4| 19.3| 3.5 | 3.2| 4.6 | -   |

Plasma sintering was quite efficient at consolidating the samples after compaction process due to very high temperature, and will improve heat transfer (free electron movement) together with ionization process in plasma [9, 10]. As the effect of the high temperature of the plasma, the green body more easily consolidated, forming necking in relatively short time compared to in conventional sintering process.

From the EDX results as presented in Table 2, in general Fe-rich phase form the alloy matrix, which appears as grey area. This phase can be recognized as ferrite since the main composition of this alloy consists of Fe-Cr-Al which is categorized as ferritic steel [11].

Another reason why the main phase formed in ODS steel is ferrite is the base elements such as Fe and Cr. Both elements are well known as ferrite formers. These elements can form Fe-Cr matrix which is a ferrite phase. Also, a recent study stated that if the addition of Cr in weight percentage reaches more than 12%, it will be categorized as ferritic steel [12]. A distinct feature found in Figure 1(a) point 2, where there is smooth and spotless region that represents Cr-rich phase which is also categorized as ferrite phase. Higher Cr content in a steel can make an alloy have dominant ferrite phase because Cr element is one of the ferrite formers [13]. Another unique feature there is also found in Figure 1(b) is the presence of white region that represents Y-rich phase. This Y-rich phase will make a compound together with O to become Y₂O₃ and this oxide particle will prevent dislocation motion at high temperature, providing resistance to creep [14]. This oxide particle is very stable at elevated temperature since it has a high melting point [15]. Nickel was identified in the microstructure of ODS steel with 2% wt of Ni and this element will be a compound with Al to create NiAl intermetallic compound. According to EDX result, with the increasing of nickel content, it will form more intermetallic compound and can
affect the resistance to high temperature [16]. To further identify phase in the specimen, X-Ray Diffraction is used to analyze formed phase.

3.2 Phase formation

Type of phases which were present in the samples were analyzed using X-Ray Diffraction, which results are shown in Figure 2.

![XRD patterns of ODS alloy with addition of (a) 0.5 wt% Ni and (b) 2 wt% Ni](image)

Based on Table 3, In the XRD patterns of ODS alloy with addition of 0.5 wt% Ni, there are 6 diffraction peaks at angles 2θ of 44.6°, 64.9°, 82.2°, 98.8°, 116.2°, and 137° with Miller indices of (110), (200), (211), (220), (310), and (222). Based on the reference, type of phase which are present is (Fe,Ni) or kamacite and has cubic crystal [17]. Another phase present is FeCrAl or ferrite. The diffraction peaks of this phase have angles 2θ of 44.6°, 65°, 82.3°, 98.9°, 116.3°, and 137.1° with Miller indices of (110), (200), (211), (220), (310), and (222) [18].

The ferrite phase is present because ODS alloy with the main composition of Fe-Cr-Al is categorized as ferritic steel [11]. According to the result of XRD analysis, there are also 6 diffraction peaks at angles 2θ which are 30.9°, 44.3°, 55°, 64.4°, 73.2°, and 81.6° with Miller indices of (100), (110), (111), (200), (210) and (211). Based on the reference, type of phase which formed is intermetallic compound of NiAl and has cubic crystal [19]. The reason that Ni is added to ODS steel in this work is to observe whether nickel aluminate phase can be formed in this alloy, as this phase can improve the resistance of oxidation at high temperature and creep due to high temperature application [20]. NiAl possesses excellent high temperature strength and resistance to oxidation and corrosion because of the long range ordered structure of this phase, and this structure impedes the mobillity of atoms [16]. This NiAl intermetallic
compound can form small precipitates, and together with oxide particle (Y$_2$O$_3$), it helps to preserve the atomic order from dislocation, especially in high temperature. Also, this intermetallic compound acts as strengthening constituent in nickel based super alloy [16, 19].

Table 3. Result of XRD Pattern for addition of 0.5% Ni.

| No | Addition Element | Diffraction Peaks (2θ) | Miller Indices | Phase          |
|----|------------------|------------------------|----------------|----------------|
| 1  | Ni 0.5%          | 44.6°                  | (110)          | Kamacite       |
|    |                  | 64.9°                  | (200)          |                |
|    |                  | 82.2°                  | (211)          |                |
|    |                  | 98.8°                  | (220)          |                |
|    |                  | 116.2°                 | (310)          |                |
|    |                  | 137°                   | (222)          |                |
| 2  | Ni 0.5%          | 44.6°                  | (110)          | FeCrAl (Ferrite)|
|    |                  | 65°                    | (200)          |                |
|    |                  | 82.3°                  | (211)          |                |
|    |                  | 98.9°                  | (220)          |                |
|    |                  | 116.3°                 | (310)          |                |
|    |                  | 137.1°                 | (222)          |                |
| 3  | Ni 0.5%          | 30.9°                  | (100)          | NiAl           |
|    |                  | 44.3°                  | (110)          |                |
|    |                  | 55°                    | (111)          |                |
|    |                  | 64.4°                  | (200)          |                |
|    |                  | 73.2°                  | (210)          |                |
|    |                  | 81.6°                  | (211)          |                |

There is no significant change between ODS alloy with addition of 0.5 wt% Ni and addition of 2 wt% Ni. Based on the results of XRD analysis in the ODS alloy with 2 wt% Ni, the phases formed are similar. There are also three type of phases, which are NiAl, (Fe,Ni) or kamacite, and FeCrAl (ferrite), although increase in nickel addition would increase the amount of NiAl phase that will give advantage in the improvement of resistance to corrosion or oxidation at high temperature [21]. Further research of oxidation or corrosion resistance to high temperature should be done to determine the effect of NiAl phase.

3.3 Hardness

Vickers micro hardness testing was used to know the relation of nickel addition to the hardness value of ODS alloy. The result is shown in Figure 3.

Based on the graph above, the increase of Ni percentage to ODS alloy will result in the increase of hardness value of the samples. The results of the hardness data are 109.37 HV for addition of 0.5 wt% Ni, 142.43 HV for addition of 1 wt% Ni, 157.17 HV for addition of 1.5 wt% Ni, and 159.9 HV for addition of 2 wt% Ni. According to references, the addition of Ni to steel alloy will increase the strength of ferrite phase, accompanied with the improvement of toughness and hardness [22]. The increase of nickel weight percentage to ODS alloy induces improvement of hardness value. Based on the result of XRD analysis, with the increasing nickel content, more intermetallic compound of NiAl formed. This intermetallic compound has similar properties to both ceramic and metal, and it is usually also used as
strengthening constituent in nickel-base super alloy for high temperature application [23]. Hardness value of the samples with NiAl phase formed can be related since NiAl can act as strengthening phase to ODS alloy. The more NiAl formed in ODS alloy, the higher hardness value of specimens is achieved. The conclusion is increasing of nickel content to ODS alloy improve the hardness value of the samples.

Figure 3. Vickers micro hardness vs nickel content result.

4. Conclusion
According to microstructure of the sintering process result, there is still porosity which lays across the samples. This is a usual phenomenon since sintering process only reduces the size and amount of porosity. Then, there are three phases which are present in the samples, FeCrAl (ferrite), NiAl and (Fe,Ni). One of the reasons for this research was to achieve the NiAl phase which can support the function of oxide particle in ODS alloy for the resistance of oxidation and corrosion also creep in high temperature environment. As the percentage of Ni in the ODS alloy increases, more NiAl will form, and the oxidation resistance becomes better. However, further research should be done to know the effect of this NiAl phase. The result of Vickers micro hardness testing indicates that with the increase of Ni addition to ODS alloy, the hardness value of samples improves because more NiAl formed in the samples which act as strengthening constituent.

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